



This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

### Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

- + *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.
- + *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.
- + *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.
- + *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

### About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at <http://books.google.com/>

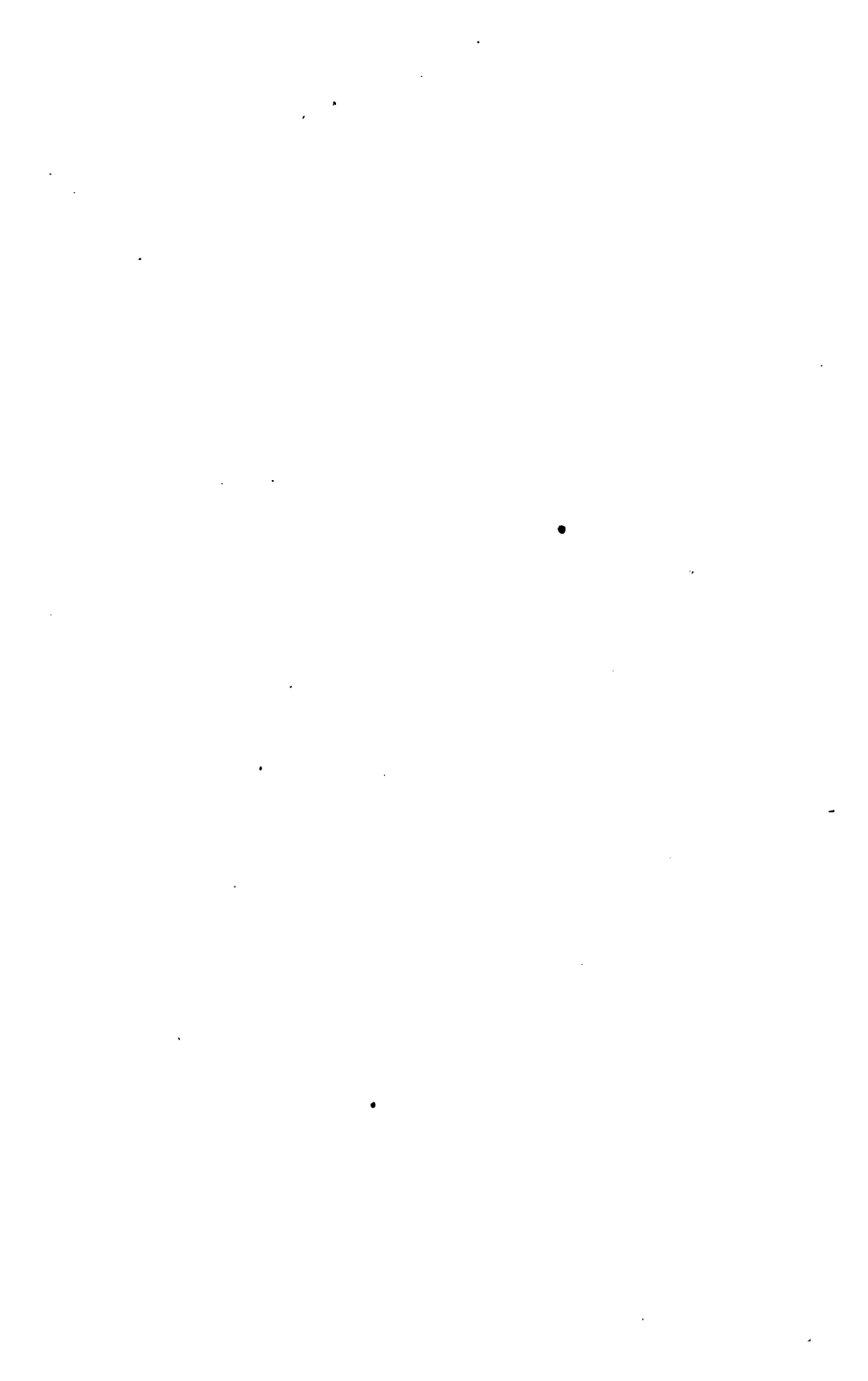
NO 17127

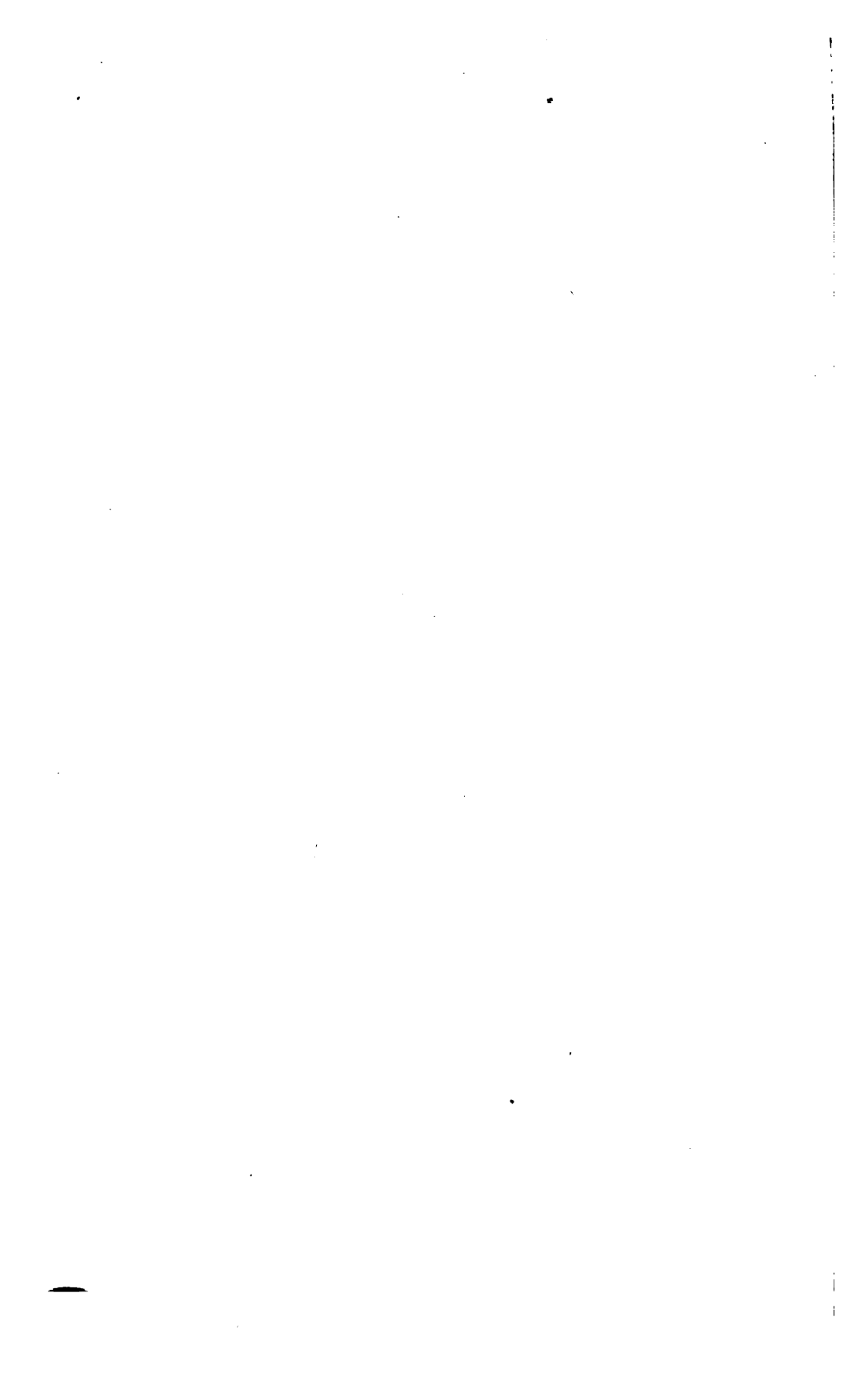
HARVARD UNIVERSITY



LIBRARY OF THE  
BIOLOGICAL LABORATORIES  
*from*  
HARVARD COLLEGE LIBRARY

MAY 4 1949







THE JOURNAL  
—OF THE—  
AMERICAN CHEMICAL SOCIETY.

---

VOLUME XVII.

1895.

---

COMMITTEE ON PAPERS AND PUBLICATIONS:

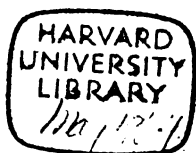
EDWARD HART, Editor,

J. H. LONG,

THOMAS B. OSBORNE.

Photolithograph Reproduction  
By Permission of The American Chemical Society

JOHNSON REPRINT CORPORATION  
NEW YORK, N. Y., U. S. A.



---

**COPYRIGHT, 1895,**  
**BY EDWARD HART, JOHN H. LONG,**  
**AND THOMAS B. OSBORNE.**  
**Committee on Papers and Publications of the**  
**American Chemical Society.**

---

PHOTOLITHOGRAPHED BY  
THE MURRAY PRINTING COMPANY  
WAKEFIELD, MASSACHUSETTS

# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

---

### THE DECARBONIZATION OF BONE-BLACK.<sup>1</sup>

BY W. D. HORNE, PH.D.

Received April 26, 1895.

THE chief value of the enormous quantities of bone-black annually used in refining sugar, glucose, mineral and other oils, etc., lies in its power to withdraw from solutions the contained organic coloring matters. After the liquid under treatment has run for some time over the bone-black, the absorption of coloring-matters by the latter is seen to diminish, and when this has proceeded to a certain point the supply is cut off, and the bone-black subsequently washed with water, naphtha, or other appropriate solvent, to wash out, as far as possible, the coloring-matters, etc., which have been absorbed by the bone-black. In spite of the most careful washing, however, some carbonaceous matter persistently clings to the char, to remove which the bone-black is heated in closed iron pipes or retorts in kilns, without the access of air. A destructive distillation of the carbonaceous matters results, driving out a large proportion of their substance in gaseous form, but still leaving a small quantity of their carbon deposited in the pores of the grains of bone-black. This accumulation of carbon is quite slow, and the char may be used about a hundred times in refining high-grade sugars before its pores become so thoroughly choked as to destroy its usefulness. The deterioration is more rapid for low-grade sugars, and in refining petroleum the deterioration is so excessive that a dozen treatments will often exhaust the char. Thus the sugar refiner finds his char about exhausted at the end of

<sup>1</sup> Read before the New York Section, April 12, 1895.

the year, and the oil refiner much sooner. Other minor changes take place in the char, of course, but none which can compare in destructiveness to this accumulation of carbon. When it is remembered that about three tons of bone-black are needed in a sugar refinery to each ton of sugar represented in the daily melt, and that while new bone-black costs upward of \$40.00 a ton the discarded char brings only about one-third of that price, it will be appreciated what a heavy annual investment the purchase of new bone-black entails.

Some unsuccessful attempts to obviate this difficulty had been made by others, but the distinction of overcoming it belongs to Mr. Moriz Weinrich, who is already world renowned as the inventor of the steam washing centrifugal machine which bears his name. He has recently invented and patented processes and apparatus for radically improving the quality of old bone-black. One process consists of the complete removal of carbon from the bone-black and the artificial introduction of fresh carbon in smaller quantity. The other consists of a uniform partial removal of carbon when that element is excessive. The first is applicable to exhausted char, such as sugar refineries and oil refineries discard. The second is preferable for removing small percentages of carbon from bone-black which has begun to deteriorate through the choking of its pores with carbon, but which has not reached the limit of usefulness. In the first case all of the carbon is burned out by passing the bone-black in a small continuous stream through the inventor's apparatus, a nearly horizontal cylinder of sheet iron, which is heated to a dull red and revolved constantly. The char enters the drum through a central orifice in the head, closing one end, which is slightly higher than the other, and leaves the drum through peripheral openings in the head of the lower end. Within the drum longitudinal projecting ribs serve to expose the bone-black more completely to the hot air in the drum. The air enters at the openings in the lower end of the drum and either wholly or partially oxidizes the carbon in the bone-black; that depending upon the heat of the drum, the volume of air, the amount of bone-black fed into the drum, the speed of turning, etc.

In case the carbon is all removed the mineral frame-work

remains intact with its pores opened up. This bone-black can then be treated with a solution of glue or molasses, or other carbonaceous matter, to thoroughly impregnate it. Then the whole can be rendered thoroughly dry and submitted to destructive distillation in closed retorts without the access of air. The organic matter is hereby charred in the very pores of the grains of bone, and the carbon thus deposited seems to be exactly similar to that originally present. After the above recarbonization the grains must be washed with hot water to remove soluble substances; and then the char is ready for use.

In the case of partial decarbonization only one operation, that of passing through the drum, is necessary, where a high carbon char can be reduced to a low carbon char and the process regulated to remove any percentage required.

Washed char, fresh from the filters and containing those organic matters which are usually destroyed by destructive distillation in retorts or kilns, can be thoroughly cleansed by passing it through this apparatus at a heat below redness, which indicates the possibility of this method's replacing the present purification or revivification in kilns.

These methods have been investigated and tested by the author, both in the laboratory and on a working scale, in their relations to sugar refining, with eminently satisfactory results, as shown below. Some unfavorable results have, at times, appeared, but they have been due to removable causes, or have been so slight as to be negligible in consideration of the great advantages attained.

#### LABORATORY TESTS ON TOTAL DECARBONIZATION, ETC.

A quantity of old bone-black, discarded from a sugar refinery, and containing in the neighborhood of twenty per cent. of carbon, was heated in the open air until it was burned white. Sufficient low-grade sugar syrup, for its dry substance to be equal to about fifteen per cent. of the weight of the decarbonized char, was diluted with hot water, thoroughly mixed with the burned bone, evaporated to dryness, and the mixture then put into an iron tube, closed at one end, and having only a small vent in the cap at the other end, and heated to a dull red until all the gas was given off. This carbonized bone was then cooled

and washed with water, to remove all soluble matter, and dried. It now resembled new char in appearance, but contained only about five per cent. carbon. Three hundred cc. of this char were put into a liter bottle with 350 cc. of a solution of molasses sugar, 33° Bé. and exponent = 89.2, and heated one and a half hours in a water-bath at 175° F., with frequent agitations. New char was washed similarly and dried, and 300 cc. subjected to the same treatment. The solutions were then filtered off, and while both had been greatly lightened in color, that from the recarbonized char was considerably lighter than that from the new char. The exponent of the former was 93.0; that of the latter 92.4. The char samples were carefully washed and heated in closed tubes, as before, to remove the impurities, and again treated as before. These two samples were submitted to nine successive treatments with very dark sugar solutions, the object being to ascertain whether the artificially carbonized char would stand use as well as ordinary char. It was also found that while both samples deteriorated greatly, owing to the large amount of work which had been put upon them, the treated char was relatively as much better than the other sample, at the end, as it had been at the beginning, so far as color was concerned. The new char had increased the exponent 0.17 per cent. more than the treated char, in the average of the nine tests, but while the new char had removed 66.6 per cent. of the color from the average solution the recarbonized char had removed 83.3 per cent.

#### FACTORY TESTS ON A WORKING SCALE.

A decarbonizing apparatus was built, consisting of a cylindrical drum of three-sixteenth inch wrought iron, nine and a half feet long by thirty inches diameter, with a central longitudinal shaft by which it is turned. The drum has a slight inclination from the horizontal and is provided with internal longitudinal ribs to raise the char a little way on the ascending side as the drum revolves. The whole is enclosed by brickwork and heated by a fire built beneath its lower end. By means of this, either a total or a partial decarbonization of char can be effected, and the amount to be burned off can be regulated to a nicety by proper adjustment.

Bone-black that had been in constant use nearly a year and containing twelve per cent. of carbon was reduced to nine per cent. of carbon and tested in the laboratory against the untreated char by the above-mentioned filtration process. The original solution used had a color = 200 on an arbitrary scale. The filtrate from the untreated char had a color = 80; that from the treated char had a color = 27.

In another test the original solution had a color of 240.

Filtrate from untreated char.....	110
"    "    treated char.....	20
"    "    over-treated char (some white grains) ..	26

The same samples of char, after draining, were treated again with a slightly less amount of sugar solution.

Filtrate from untreated char,	color = 120
"    "    treated char,	" = 40
"    "    over-treated char,	" = 50

In the two treatments the untreated char removed 52.5 per cent. of the color, the treated char 87.9 per cent., and the over-treated char 84.5 per cent.

It was thought that these tests extending over one and a half or two hours might show a greater difference between the samples than tests extending over a longer period, and so the following experiment was made. Three hundred cc. of each char were heated at 175°F., with 600 cc. Muscovado sugar solution at 27° Bé. giving the following results:

Original solution had a color = 210

	One and a half hours.	Six hours.
Filtrate from house char.....	50	12
"    "    new char .....	40	10
"    "    treated char.....	20	7

showing that the treated char held its own very satisfactorily.

Further, a series of six consecutive treatments of new char, char several months in use, and the same after partial decarbonization was made. Three hundred cc. of each black were heated at 175°F. with 600 cc. Muscovado solution of 27° Bé. for ten hours, being shaken every fifteen minutes. The char was thoroughly washed, and heated in nearly closed tubes after each absorption test. The average color of the liquor going on was 152.5; that coming off was, house char, 22.8; new char, 16.4; treated char,

16.7. The treated char, although a trifle below the new char in the final average, actually deteriorated less during the tests than either of the others, and thus showed a relative improvement at the end of the experiment.

Many tests have been made on the working scale which have demonstrated the superiority of the decarbonized char over old char, and its equality in many respects to new char.

In the first of these tests a filter of house char containing 12.32 per cent. carbon, and another of decarbonized char containing 10.04 of carbon, had equal quantities of the same liquor run over them for a prolonged period, forty-nine and a fourth hours. The average liquor from the house char had a color of 25, while that from the treated char had an average color of only 15; and it was very striking that the difference in color increased as the test proceeded, the latter part of the liquor from the untreated char averaging 50, while the corresponding portion from the treated char averaged only 25. The house char withdrew 79.88 per cent. of the color present, while the treated char withdrew 87.69 per cent.

In another set of filtrations on the working scale, in a sugar refinery, a raw sugar solution, color 120 and  $27.7^{\circ}$  Bé., and exponent 90.09, was put, in the regular course of running, through filters of char respectively several months old, new, and decarbonized. The average color of that from the old char was 23; from new char, 19; from decarbonized char 18. The exponents scarcely varied, being 92.17, 92.37, and 92.09, respectively.

These are a few of a great many tests both in the laboratory and in the factory made upon char which had been partially decarbonized in a small working model which could not be controlled with the desired nicety. While the average per cent. of carbon in the decarbonized char was 10.04 per cent., or 2.28 per cent. less than in that from which it was prepared, there was a good deal of it which through different causes still contained more than eleven per cent. of carbon, and considerable which had been so over-heated as to be rendered weak as a decolorizer. These two extremes, while giving a favorable-looking average per cent. of carbon, both deteriorate the char for the purposes in hand.



Some improvement having been made in the operation of the decarbonizing drum, which, however, is still far inferior to what the inventor's design calls for, it has been possible to turn out a much more uniform product. The carbon can be reduced to any desired point and kept to within half a per cent. of the requisite figure. Having thus prepared another large quantity of char, sufficient for factory tests, another experiment was made. The carbon this time was reduced from 13.03 per cent. to 10.22 per cent., and two filters filled with these grades were run against each other. The liquor entering had a color of 110. The average of that coming from the untreated char was ten, while that coming from the treated char, all the conditions being carefully kept precisely similar, was only five. From the old char the liquor ran water-white for less than an hour; from the decarbonized char it ran water-white for more than five hours; and at the end of the run the liquor from this filter was only about as dark as that at the middle of the run from the filter of ordinary char.

Now, as to the changes in the bone-black itself: after a partial decarbonization, microscopic examination shows the decarbonization to be uniform throughout the grain. Two analyses made to illustrate the chemical changes may be quoted:

	Before decarbonization.	After decarbonization.
Carbon.....	12.32	8.90
Calcium carbonate.....	3.32	3.26
Iron .....	0.32	0.21
Calcium sulphate.....	0.904	0.877
Calcium sulphide.....	0.628	0.494

The most noticeable and, in fact, the most desirable changes are the reduction of carbon, with a corresponding opening of the pores and increase in absorbing power; and the reduction of calcium sulphide, which is very important for sugar refineries, in view of the deleterious action this latter substance exercises upon the sugar.

Numerous experiments showed that the calcium carbonate is not decomposed by the mild heat which suffices for oxidizing the carbon, and the slight decrease indicated above is doubtless due to variations in samples or error of analysis.

The friction of the grains of bone-black against each other in

the drum is so slight that very little dust is formed. Samples taken to represent as nearly as possible the same char before and after treatment showed per cents. of dust as follows :

	Before treatment.	After treatment.
Finer than thirty mesh....	12.56	12.64
"    "    fifty    "    ....	0.96	2.20

The bone-black becomes specifically lighter in proportion to the carbon lost, but this does not show in the determinations of specific gravity, probably because of the grains packing more closely after treatment. This indicates a wearing off of some sharp corners of the grains. A quantity of bone-black which, before treatment, had a sp. gr. = 1.0624, and lost 2.81 per cent. of carbon during treatment, had a sp. gr. = 1.0636 afterward.

As might be expected, the process of opening the choked pores renders the bone-black slightly more friable, as shown by the fact that a sample which, before treatment, gave 1.76 per cent. of dust, by the method described by the author in a previous paper (This JOURNAL, January, 1895), gave 2.84 per cent. after treatment. This, however, is scarcely more than is given by some new bone-blacks.

The great advantages of these inventions, then, are quite apparent. The refiner of oil, sugar, or glucose, who uses large quantities of bone-black need not discard it at a great loss after its pores are choked with carbon and its decolorizing power lost; but he can, by a very simple and inexpensive process, bring it back to its original decolorizing power, when it will last nearly, if not quite, as long as before. But by far the greater advantage is the possibility of preventing its ever getting into bad condition, by submitting it to the decarbonizing process while yet the carbon is only slightly above the normal for new char, and thus keeping it always at its maximum efficiency.

By a careful use of this apparatus it is possible to burn off the organic impurities persisting in bone-black after washing, instead of charring them as in the ordinary method of revivifying, in kilns with the exclusion of air; and it is not at all impossible that the apparatus will, in the near future, supersede the present kilns used in all factories employing large quantities of bone-black.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

## SULPHIODIDE OF LEAD.

BY VICTOR LENHER.

Received March 30, 1895.

ACCORDING to Humefeld (*J. prakt. Chem.*, 7, 27) Reinsch (*J. prakt. Chem.*, 13, 130) and Parmentier (*Compt. rend.*, 114, 299) there exists a chloresulphide of lead and an analogous bromsulphide of a cinnabar red color, obtained by adding hydrogen sulphide to a solution of lead chloride in hydrochloric acid, or to the corresponding bromide in hydrobromic acid.

As lead iodide dissolves readily in potassium iodide with the formation of the double iodide  $\text{PbI}_2 \cdot 2\text{KI}$ , and with excess of potassium iodide  $\text{PbI}_2 \cdot 4\text{KI}$ , it was found that when working with this salt an iododisulphide of brick-red color and rapidly changing composition was formed when its solution was treated with hydrogen sulphide.

The precipitate formed, when hydrogen sulphide is added to a solution of the double iodide in potassium iodide, is brick-red in color, rapidly changing, on further addition of that reagent, successively through dark red to brown, and finally the black sulphide is obtained which careful examination showed to be free from iodine. Cold water saturated with hydrogen sulphide was added to a strong solution of lead iodide in a saturated solution of potassium iodide; the red precipitate which was obtained was rapidly filtered by means of a suction apparatus, washed with a saturated solution of potassium iodide to remove any  $\text{PbI}_2 \cdot \text{KI}$  which possibly may have separated by the dilution; it was then washed with cold water till the reaction for iodine entirely disappeared; absolute alcohol was then added to displace the water, followed by carbon bisulphide to remove any sulphur, after which absolute alcohol was again added and the precipitate dried by drawing cold air over it.

When  $\text{PbI}_2 \cdot 4\text{KI}$  is diluted with water, yellow  $\text{PbI}_2 \cdot \text{KI}$  separates. The red sulphide was examined very carefully for potassium but none was found.

As the tendency of the substance to decompose into lead sulphide and lead iodide was so great, only small quantities were prepared at one time.

The lead was determined by treatment with nitric acid, followed by a few drops of sulphuric, and was weighed as sulphate. The sulphur was determined only after much trouble, as all attempts to oxidize it caused sulphur to separate. The method employed was treatment with a hot solution of sodium carbonate, which completely converted it into lead sulphide, carbonate, and sodium iodide. This was brought upon a Gooch crucible, washed with water, followed by a little dilute acetic acid to remove the carbonate, again washed with water, after which it was treated with nitric and sulphuric acids, and weighed as lead sulphate.

The iodine was estimated by covering the iodosulphide with an excess of a decinormal solution of silver nitrate; decomposition was then effected by means of nitric acid, and the excess of silver titrated with a decinormal ammonium thiocyanate solution, using ferric alum as an indicator. Analysis gave the results :

Lead.	Iodine.	Sulphur.
49.06	49.97	1.51
50.16	49.81	1.98
.....	50.24	2.21
.....	50.33	2.17

The results approximate the composition of  $\text{PbS}_4\text{PbI}_4$ , which requires :

Lead.	Iodine.	Sulphur.
49.20	48.77	1.53

Hydrogen sulphide gas passed through a saturated solution of  $\text{PbI}_2, 4\text{KI}$  in the cold, also gave a brick-red precipitate which, treated in the manner described in the previous experiment, gave on analysis, 49.98 per cent. of iodine.

This method for the preparation of the iodosulphide is very unsatisfactory, as it rapidly darkens even in presence of large excess of the iodide, and from the fact that only a small fraction of a per cent. of product can be obtained.

Various colored products were obtained in the investigation,

containing lead from 49.06 per cent. to the normal sulphide, and iodine in a similar manner from 50.84 per cent. to a sulphide entirely free from it. All of these but the one approximating,  $\text{PbS}_4\text{PbI}_2$ , were inconstant in composition and more or less rapidly decomposed into lead sulphide and lead iodide, as might be expected from the knowledge of the chlor- and bromsulphides; the iodosulphide is readily decomposed by heat, acids, and alkalies; and even long exposure to light decomposes it.

### ON THE DETERMINATION OF SMALL QUANTITIES OF PHOSPHORIC ACID BY THE CITRATE METHOD.<sup>1</sup>

BY E. G. RUNYAN AND H. W. WILEY.

Received April 15, 1895.

THE results obtained by analysts in different parts of the world in precipitating phosphoric acid directly by magnesia mixture, in presence of citric acid or its salts, show that this process may safely take the place of the molybdenum method with all standard tricalcium phosphates or their preparations. We have observed in our work the most satisfactory agreement between this method and the molybdenum method of the Association of Official Agricultural Chemists. This statement, however, holds true only when the phosphoric acid is present in considerable quantities, at least in excess of five per cent. With smaller quantities of phosphoric acid we have observed that the citrate method leads to results which are decidedly inferior to those obtained by the molybdenum process.

The principle of the citrate method may be stated as follows: In the presence of a considerable excess of ammonium citrate a solution of a magnesium salt, made alkaline by ammonia, will precipitate the phosphoric acid as ammonium magnesium phosphate. The iron and alumina which may be present in the solution will not be precipitated under the above circumstances either as hydroxides or as phosphates. The ammonium magnesium phosphate can be subsequently separated by filtration, converted into magnesium pyrophosphate and weighed. An examination of the

<sup>1</sup> Read before the Washington Section, April 11, 1895.

pyrophosphate obtained as above will disclose the presence of iron and alumina, but experience has shown that an equivalent amount of phosphoric acid will be found in the filtrate after the separation of the ammonium magnesium phosphate. The errors are, therefore, mutually compensatory and results obtained agree within the ordinary errors of analysis with those of the molybdenum method.

Our experience having shown us that the above principles could not be applied in the presence of small quantities of phosphoric acid we were led to try the following simple expedient: Whenever we had to deal with a small percentage of phosphoric acid, for instance, anything below ten per cent., we added to the solution, before the precipitation, a sufficient quantity of a solution of a phosphate of known strength to bring the total percentage of phosphoric acid in the mixture up to that of a natural tricalcium phosphate of good quality; *viz.*, from fifteen to thirty per cent. In these circumstances we were able to obtain perfectly accurate results, even in cases where less than one per cent. of phosphoric acid was present. The following analytical data will illustrate the character of the work:

*Solutions Employed.*—No. 1. This is a solution of cottonseed-meal and castor pomace. It is part of a sample sent out last year, by the reporter on phosphoric acid, to the members of the Association of Official Agricultural Chemists.

Nos. 2 to 5 inclusive. These are solutions of natural phosphates containing very small percentages of phosphoric acid, some of them less than one per cent.

Nos. 6 to 10 inclusive. These are preparations made by diluting a standard solution of a superphosphate with water. This superphosphate was a part of a sample sent out by the official reporter for 1894.

Nos. 11 to 17 inclusive. These are natural rock phosphates containing large percentages of phosphoric acid, and the data show the agreement between the direct citrate and the official molybdenum method.

The above solutions for the citrate method were made by treating two grams of the material with fifty cc. of sulphuric acid and

twenty cc. of nitric acid, and boiling until fumes of sulphuric acid began to escape.

## CITRATE METHOD.

Solution No.	Direct. Per cent. $P_2O_5$ .	After adding 25 cc. of known phos- phate solu- tion.		Official molybdenum method. Per cent. $P_2O_5$ .
		Per cent. $P_2O_5$ .	Calculated for original solution. Per cent. $P_2O_5$ .	
1.	1.08	8.93	2.51	2.46
	2.17 <sup>1</sup>	8.97	2.55	2.50
	1.53	15.92	2.61	2.49
	2.30 <sup>1</sup>	15.76	2.45	2.48
2.	0.76	10.91	0.89	1.02
	0.64	11.10	1.08	1.02
3.	3.76	14.10	4.08	4.08
	3.64	14.16	4.14	3.99
4.	0.32	10.78	0.76	0.77
	0.19	10.91	0.89	0.76
5.	0.25	10.82	0.80	0.88
6.	0.76	11.16	1.14	1.15
	0.96	11.16	1.14	1.15
7.	2.17	12.38	2.36	2.30
	2.36	12.31	2.29	2.31
8.	3.25	13.46	3.44	3.44
	3.25	13.46	3.44	3.46
9.	4.40	14.67	4.65	4.62
	4.47	14.48	4.46	4.59
10.	5.68	15.69	5.67	5.74
	5.29	15.63	5.61	5.77
11.	17.23	....	....	17.29
12.	37.77	....	....	37.77
13.	15.37	....	....	15.44
14.	29.16	....	....	29.22
15.	29.49	....	....	29.47
16.	31.64	....	....	31.64
17.	32.22	....	....	32.15

*Explanatory Notes.*—With solution No. 1 four determinations were made. In the first and third instances the mixture was allowed to stand twenty-four hours before filtering, while in the third and fourth instances it was allowed to remain for three days. The results clearly show the progressive separation of the crystalline precipitate, almost the full quantity being secured after the lapse of three days. In the first and second instances there was added enough of a solution of rock phosphate to bring the total phosphoric acid up to about nine per cent., while in the third and fourth determinations a solution of a richer rock was added, bringing the total phosphoric acid in the mixture up to about sixteen per cent. There was little difference noted in the

<sup>1</sup> Stood 72 hours.

results. Beginning with solution No. 2, the increase in the content of phosphoric acid was secured by adding measured quantities of a solution of ammonium phosphate of known strength. The results show that a chemically pure phosphate can be used with equal safety in place of solutions of rock phosphate. By a study of the results obtained with solution 10, it is seen that when the content of phosphoric acid reaches about six per cent. the direct method with magnesium citrate gives approximately correct results. It is to be recommended, however, in all cases where the sample contains less than ten per cent., that fortification with a solution of a phosphate of known strength be practiced.

Solutions 11 to 17 inclusive were made from samples of rock phosphate quite rich in phosphoric acid and, therefore, required no fortification. It is seen in all cases that the data obtained by the direct citrate method are almost identical with those secured by the official molybdenum process.

*Conclusions.*—(1) In all cases of samples of tricalcium phosphate, or acid phosphates made therefrom, containing the usual accompanying substances, the phosphoric acid may be correctly estimated by direct precipitation with magnesium citrate.

(2) In all cases of the analysis of natural rock phosphates containing less than five per cent. of phosphoric acid it is necessary to fortify the solution before precipitation by adding a measured quantity of a solution of phosphoric acid of known strength.

(3) The fortifying solutions employed may be made either from natural tricalcium phosphates or from chemically pure phosphate salts.

(4) The direct precipitation of the phosphoric acid in the presence of ammonium citrate by ammoniacal magnesia mixture is a quicker and less expensive process than the official molybdenum method and leads to results equally accurate.

(5) We have not applied the direct citrate method to the natural iron and aluminum phosphates, and therefore can make no statement in regard to its accuracy in the treatment of such samples.



[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF OBERLIN  
COLLEGE.]

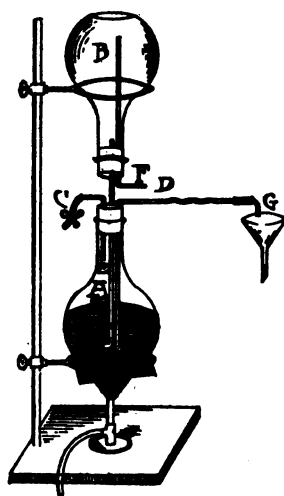
## AN ARRANGEMENT FOR WASHING PRECIPITATES WITH BOILING WATER.

BY FRANK F. JEWETT.

Received February 7, 1895.

IN using the ordinary wash-bottle for boiling water, the mouth-piece is not infrequently so much heated by escaping steam that the lips, when applied to it in the usual manner, are either uncomfortably overheated or positively burned. To avoid this result the apparatus, herein described, was devised, and has worked with perfect satisfaction.

Two flasks are arranged as shown in the figure. To the lower one, A, is fitted a rubber stopper through which pass three glass tubes. A short one, bent at right angles, just enters the flask, and to its outer extremity is attached a short rubber tube provided with a spring clip C.



A long tube reaches to the bottom of the flask and extends six or eight inches at right angles from a point just above the stopper. To its outer end is attached a rubber tube a few inches long, into which is fitted a glass jet, G, bent at right angles and wound about with a strip of felt or other non-conducting material. A third tube, E, extends from the bottom of the lower flask just through the stopper of the upper flask B, which is also provided with the tube F reaching to the top of the flask.

To use the apparatus, the water is heated to gentle boiling, the steam passing out through the open clip C. When a precipitate is to be washed, the clip is closed and the pressure of the steam at once drives the water out through the tube D. By clamping the non-

conducting cover of the jet G with the thumb and finger, the stream of boiling water may be directed to any place desired. Any excess of pressure simply drives the water slowly through the tube E into the upper flask, from which the air escapes through F.

When a sufficient quantity of water has been used, the clip is opened, the jet G raised, and the water immediately returns to the lower flask.

OBERLIN, OHIO.

## INTERPRETATION OF SOME RESULTS IN THE ANALYSIS OF EXTRACTS OF FUSTIC.

BY CHARLES S. BOYER.

Received April 13, 1895.

SOME time since, the writer made several analyses of samples of extract of fustic, the method of whose manufacture was at the time unknown. Since there are no recorded analyses of extracts of fustic, so far as I can find, it was thought that a statement of the results and conclusions might be of interest to those engaged in this line of work.

The method of analysis employed is briefly as follows: Five to six grams of the extract were carefully dried in a water-bath until no further loss occurred, the loss being regarded as water. Two to four grams of this dry powder was now put into a Soxhlet extractor and thoroughly and repeatedly exhausted with *absolute* alcohol, the alcoholic extract distilled, and the residue dried and weighed. The residue was in every case treated with boiling water and tested for *morin* and *maclurin* (*morin-tannin*), the former by adding to one portion a few drops of aluminum sulphate and the latter by adding to another portion some ferric chloride, but in each case with negative results. The residue from the alcoholic extract was ignited in a platinum crucible and the ash subtracted from the matter soluble in absolute alcohol. For the ash percentage, five grams of the powder was carefully ignited in a capacious platinum crucible and the resulting ash weighed.

The results of the analysis of three extracts of fustic found upon the market, together with those of two extracts whose methods of manufacture were known, are put into a table below.

The results are also calculated upon a dry basis so that they may be compared the better.

	I.			II.			III.			IV.			V.		
	Per cent.	On dry basis.	Per cent.	Per cent.	On dry basis.	Per cent.	Per cent.	On dry basis.	Per cent.	Per cent.	On dry basis.	Per cent.	Per cent.	On dry basis.	Per cent.
Water.....	67.09	....	50.42	....	36.48	....	49.62	....	6.18	....					
Organic matter soluble in absolute alcohol.....	31.34	95.23	38.57	77.79	52.85	83.20	47.41	94.11	75.55	80.53					
Ash.....	0.52	1.58	5.54	11.18	1.24	1.95	1.05	2.08	7.62	8.12					
Organic matter insoluble in alcohol.....	1.05	3.19	5.47	11.03	9.43	14.85	1.92	3.81	10.65	11.35					
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00					

Sample IV was made in an open extractor, the water used in the extraction being brought to a boil before it was run on the wood and the length of time that each "water" remained in contact with the wood being fifteen minutes. Eight "waters" were taken off. Sample V was extracted under five pounds pressure, using seven waters and the weak liquor being evaporated to dryness.

It will be seen that Sample I is very similar to IV, while the analysis of II and V are very much alike, especially in that both have a high percentage of ash and approximately the same amounts of organic matter insoluble in alcohol.

It is quite true that different brands of fustic, and even different cargoes of the same brand, contain varying percentages of inorganic matter, or ash. This might lead one to erroneous conclusions were one to depend entirely upon the ash percentages. However, the chief mineral constituents of fustic are lime and magnesia, and as a result of a large number of analyses the writer finds that these two ingredients form another guide in determining the method of extraction. The more pressure used in the extraction, the higher, within certain limits, the ash percentage, and also the larger the amount of lime and magnesia contained in the ash. In the extracts under investigation the percentages of lime and magnesia together were in I, 41.16 per cent.; IV, 46.83 per cent.; II, 68.12 per cent.; and V, 62.15 per cent. of the total ash.

Another ingredient which might prove misleading is extract of quercitron bark. In order to ascertain whether any of these extracts contained this adulterant, a series of dye-tests were

made depending upon the different affinities of the coloring principles of bark and fustic for alum and tin mordants, but in none of them could any admixture with quercitron bark extract be detected.

The conclusions drawn from these analyses and comparisons were that I was made entirely by the "open-extraction" method; II was made by the "closed-extraction" method, using five to eight pounds pressure; and that III was extracted in open vessels, but that the changes of "waters" was done under pressure. The reason for the latter conclusion was that, while the ash percentage was low, the "extractive matter," or organic matter insoluble in alcohol was very high and the only way that this could happen would be by opening up the fiber of the wood, as is the case in open boiling and then applying pressure, which carried this "extractive matter" into the extracting liquor. These conclusions were subsequently borne out by experiments.

CAMDEN, N. J., April 6, 1895.

## THE TUNGSTATES AND MOLYBDATES OF THE RARE EARTHS.

BY FANNY R. M. HITCHCOCK.

[Continued from page 494.]

*b.* Five cc. of the cerium sulphate solution were diluted to sixty cc., and brought to boiling, when alcohol was added, five cc. at a time, until sixty-five cc. had gone in, but the solution still remained clear. To this hot solution the cerium sulphate solution was added in the same way as the alcohol had been. The first addition of five cc. caused a precipitate to form, which redissolved at once. The second addition of five cc. caused a precipitate which dissolved again very slowly, and with the third addition the cerium sulphate came down in fine needles.

It was evident that the amount of alcohol which had been used in experiments 8, 9 and 10, with the sodium molybdate, had not been sufficiently great to cause by itself the precipitation of the cerium sulphate. The experiments were, therefore, repeated, the conditions being slightly varied.

*Experiment 11.* Ten cc. sodium molybdate solution were diluted to 100 cc., and fifteen cc. of the cerium sulphate solution added. To this, in the cold, fifty cc. of ninety-five per cent. alcohol were added very gradually, and with constant stirring. The

whole was allowed to stand for half an hour, when the precipitate was filtered off, washed, first with fifty per cent. alcohol, then with thirty per cent., and finally with pure water, ignited, and weighed. The results obtained were the best of all the series.

Wt. obtained.	Calculated.	Difference.
0.1620 gram.	0.1629	—0.0009

The ignited precipitate dissolved in hydrochloric acid gave no trace of sulphuric acid when tested with barium chloride.

*Experiment 12.*—This was a duplicate of No. 11, except that the final washing was done with twenty per cent. alcohol instead of pure water. The washing was continued until there was no reaction with barium chloride for sulphuric acid.

Wt. obtained.	Calculated.	Difference.
0.1799 gram.	0.1629	+0.0170

The precipitate was tested as before, and proved to contain cerium sulphate.

*Experiment 13.*—Ten cc. of sodium molybdate solution were diluted to 185 cc. and fifty cc. of ninety-five per cent. alcohol added, followed by fifteen cc. of cerium sulphate solution. After standing an hour the precipitate was filtered off, and washed in the same manner as in No. 12.

Wt. obtained.	Calculated.	Difference.
0.1644 gram.	0.1629	0.0015

From the precipitate barium sulphate equivalent to 0.00146 gram of cerium sulphate was obtained, and the filtrate gave 0.0007 gram of molybdenum trisulphide.

*Experiment 14.*—This was a duplicate of No. 13.

Wt. obtained.	Calculated.	Difference.
0.1708 gram.	0.1629	0.0079

The precipitate yielded the equivalent of 0.0090 gram of cerium sulphate with barium chloride.

With hydrogen sulphide a precipitate of molybdenum trisulphide was given by all the filtrates from the experiments described above, the amount varying in wide limits. While alcohol diminished the solubility of the cerium molybdate formed, the advantage gained was more than counterbalanced by the tendency of the molybdate to carry down with it cerium sulphate in the presence of alcohol.

## SODIUM TUNGSTATE AND CERIUM SULPHATE.

The solution of sodium tungstate used contained 27.07 grams in one liter. But few experiments were made, the results obtained being similar to those with sodium molybdate. Precipitation in a water solution alone was very incomplete, the precipitate persistently running through the filter, so that no definite results could be obtained in this way. When alcohol was used better results were obtained, the filtrate coming through clear.

*Experiment 1.*—Ten cc. sodium tungstate solution were diluted to 100 cc. with distilled water, and twenty-five cc. of ninety-five per cent. alcohol added. The whole was brought to boiling when twenty-five cc. cerium sulphate solution were added. A dense, flocculent yellow-white precipitate came down at once, subsiding rapidly; it was filtered and washed with twenty-five per cent. alcohol.

Wt. obtained.	Calculated.	Difference.
0.3266 gram.	0.3144	0.0122

*Experiment 2.*—Ten cc. of sodium tungstate solution were diluted with distilled water to 100 cc. and twenty-five cc. of ninety-five per cent. alcohol added, followed by twenty-five cc. of cerium sulphate solution in the cold. A bluish white precipitate formed, which on standing acquired a yellow tint. This was filtered cold and washed with twenty-five per cent. alcohol.

Wt. obtained.	Calculated.	Difference.
0.3125 gram.	0.3144	—0.0019

*Experiment 3.*—Ten cc. of sodium tungstate solution were diluted to 100 cc. and twenty-five cc. of ninety-five per cent. alcohol added. The whole was brought to boiling and twenty-five cc. cerium sulphate added. The precipitate was washed with hot twenty-five per cent. alcohol.

Wt. obtained.	Calculated.	Difference.
0.3322 gram.	0.3144	0.0178

The precipitate from all three solutions contained cerium sulphate, and the filtrates all showed traces of tungsten.

The next salts taken up were the two very rare ones, neodymium chloride and praseodymium chloride. For the material used I am indebted to the courtesy of Professor Waldron Shapleigh, of the Welsbach Light Company, Gloucester, N. J. The material given me consisted of the oxides prepared from the

oxalates by ignition. These oxides are considered by v. Welsbach<sup>1</sup> to be the peroxides, and the formulas  $\text{Nd}_2\text{O}_5$  and  $\text{Pr}_2\text{O}_5$  have been assigned to them.

$\text{Nd}_2\text{O}_5$  is a light brown powder, while  $\text{Pr}_2\text{O}_5$  is dark brown, almost black. Both dissolve readily in hydrochloric acid with evolution of chlorine, and form sesquichlorides. Neodymium chloride,  $\text{Nd}_2\text{Cl}_6$ , forms a rose colored solution while the corresponding praseodymium salt is pale green in color. The solutions used were prepared by evaporating the chlorides prepared from the oxides to dryness, taking up with water and again evaporating until all the hydrochloric acid was expelled. The residue was dissolved in water and filtered off from a little insoluble material which was probably a basic salt. About half a gram of the oxide was taken, and from it 100 cc. of the chloride solution was prepared.

The tungstates obtained from these salts by precipitation with sodium tungstate were gelatinous, and very difficult to filter and wash, showing a strong tendency to pass through the pores of the filter-paper.

For this reason a double filter was always used, and even with this precaution it was necessary to use as little pressure as possible with the filter-pump, and yet secure filtration. Even with the filter-pump the washing was very slow, and generally consumed a day at least, sometimes longer, although the quantities of material used were very small. The best results were obtained by washing first by decantation, and then on the filter.

The molybdates are gelatinous when first precipitated, but on heating they gradually become granular, and are then easily filtered and washed.

The neodymium tungstate has a very pale rose tint before ignition, which changes to a lavender color after ignition. The praseodymium tungstate has a decided greenish yellow tint both before and after ignition. The colors of the molybdates were similar to those of the tungstates, but deeper in tint.

The tendency of the precipitates to adhere to the sides of the beaker was a serious source of error at first; particularly after boiling, when it seemed impossible to remove them entirely. If not heated above  $70^\circ \text{C}$ . a piece of moist filter will remove the

<sup>1</sup> *Monatsh.*, 6, 477, 1885.

adherent precipitate better than anything; in most cases it removes it perfectly, while a rubber is useless.

The ignitions were all made with free access of air, and were continued for at least two hours. Apparently no reduction of the molybdic acid takes place, as a second ignition after moistening with ammonium nitrate or with nitric acid, causes no change in the weight.

The solubilities were determined by the Victor Meyer method.<sup>1</sup> It will be noticed that with the praseodymium salts the solubility increases with a rise in temperature, the increase being more marked with the tungstate than with the molybdate.

With neodymium tungstate the solubility decreases as the temperature rises, while with the molybdate it increases under the same conditions. Slight though the solubility is, it is sufficiently great to cause decided error in the results when such small quantities are taken as were used in the experiments here recorded.

It was found very difficult at first, when analyzing the salts, to obtain a constant weight for the oxides, the results being all higher than theory required. The method finally adopted proved very satisfactory. The precipitated oxalate was strongly ignited together with the filter-paper, in a covered platinum crucible, for half an hour, cooled, and moistened with saturated solution of oxalic acid, then ignited again in the covered crucible.

The excess of weight in the earlier analyses being greater than was called for by oxidation to the peroxides,  $\text{Nd}_2\text{O}_5$  and  $\text{Pr}_2\text{O}_5$ , the following experiments were made to determine how much oxygen would be taken up by the oxides after they had been reduced to the sesquioxides. In the analyses of neodymium molybdate, the theoretical amount required for the quantity taken was 0.0865 gram; the amount obtained was 0.0863 gram. This was heated in a platinum crucible with a Bunsen burner, the flame being applied at the back of the crucible, while the oxide was drawn forward to prevent any action of reducing gases, as far as possible. The cover of the crucible was bent and placed so as to cause a current of air to pass over the oxide.

<sup>1</sup> *Ber. d. chem. Ges.*, 8, 998, 1875.



From time to time the crucible was cooled and weighed. The following table shows the gain in weight observed and the length of time for which the heat had been applied. It is assumed that the weight first taken represents the sesquioxide, and the atomic mass is taken as 140.5.

Time of heating.	Weight.	Gain.	Oxide.
0 hours.	0.0863 gram.	0.0000	$\text{Nd}_2\text{O}_3$ .
4 "	0.0888 "	0.0025	$\text{Nd}_4\text{O}_7$ .
5 "	0.0892 "	0.0029	
7½ "	0.0906 "	0.0043	$\text{Nd}_2\text{O}_4?$
10½ "	0.0937 "	0.0074	
16 "	0.0958 "	0.0095	
22 "	0.0997 "	0.0134	$\text{Nd}_2\text{O}_6?$
27½ "	0.1035 "	0.0172	$\text{Nd}_2\text{O}_7?$
30½ "	0.1036 "	0.0173,	

The oxide on first heating changed to light brown, the color of the superoxide prepared by the Welsbach Company; as the heat was continued it grew lighter in color, until, when it had attained its maximum weight, it was almost pure white.

If the flame be placed directly under the oxide, it loses weight and gradually passes into the brown "superoxide,"  $\text{Nd}_4\text{O}_7$ .

A similar experiment with praseodymium sesquioxide,  $\text{Pr}_2\text{O}_3$ , gave the following results :

Time of heating.	Weight.	Gain.	Oxide.
0 hours.	0.0668 gram.	0.0000	$\text{Pr}_2\text{O}_3$ .
4 "	0.0706 "	0.0038	$\text{Pr}_2\text{O}_4?$
6 "	0.0722 "	0.0054	
8 "	0.0730 "	0.0062	$\text{Pr}_2\text{O}_5?$
11 "	0.0745 "	0.0077	
13 "	0.0749 "	0.0081	

The atomic mass of praseodymium is taken at 143.5. The color of the oxide changed in the same way as that of neodymium, passing rapidly into the black peroxide  $\text{Pr}_2\text{O}_4$  of Welsbach, then slowly changing to a reddish brown, and gradually becoming quite light in color. Whether it would be possible to increase the weight still more by heating small quantities for a long period of time, can only be determined by experiment; but the indications point to the existence of praseodymium trioxide  $\text{Pr}_2\text{O}_5$ , as the increase in weight obtained is greater than that required for  $\text{Pr}_2\text{O}_4$ .

It would appear that the oxide  $\text{Nd}_2\text{O}_3$  can be formed, improbable as it may seem, and that it is comparatively stable.

If it is really  $\text{Nd}_2\text{O}_3$ , neodymium is properly classed with manganese in the seventh group. It would be interesting to know if by reduction the monoxide  $\text{NdO}$  could also be formed.

#### SODIUM TUNGSTATE AND PRASEODYMIUM CHLORIDE.

The solution of sodium tungstate contained five grams in one liter.

*Experiment 1.*—Ten cc. of the sodium tungstate solution were diluted to 100 cc. with distilled water, and twenty-five cc. of ninety-five per cent. alcohol were added, followed by five cc. of praseodymium chloride solution in the cold. A precipitate formed at once, and the whole was boiled for an hour. It was then filtered, washed with hot water containing twenty-five per cent. of alcohol, ignited, and weighed.

Wt. obtained.	Calculated.	Difference.
0.0579 gram.	0.0586	—0.0007

*Experiment 2.*—Ten cc. of the sodium tungstate solution were diluted to 100 cc. with distilled water, and twenty-five cc. of alcohol added. The whole was brought to boiling, and five cc. of the praseodymium chloride solution added, after which the boiling was continued for an hour. The precipitate was then filtered off, and washed with cold water containing twenty per cent. of alcohol. The filtrate showed a slight opalescence, which was not removed by refiltering.

Wt. obtained.	Calculated.	Difference.
0.0540 gram.	0.0586	—0.0046

*Experiment 3.*—Twenty cc. of the sodium tungstate solution were diluted with seventy-five cc. of distilled water, and five cc. of the praseodymium chloride added. The whole was then boiled for an hour, allowed to cool, and filtered cold, the washing being done with cold water.

Wt. obtained.	Calculated.	Difference.
0.1091 gram.	0.1172	—0.0081

*Experiment 4.*—Twenty cc. of sodium tungstate solution were diluted to 100 cc. with distilled water, and five cc. of the praseodymium chloride solution added. The whole was allowed to

stand for twelve hours, then brought to boiling, filtered hot, and washed with boiling water.

Wt. obtained.	Calculated.	Difference.
0.1136 gram.	0.1172	—0.0036

The filtrate was boiled for an hour with fifty cc. of ninety-five per cent. alcohol, but no additional precipitate was obtained.

*Experiments 5 and 6.*—Twenty cc. of the sodium tungstate solution were diluted to 100 cc. with distilled water, and five cc. of the praseodymium chloride solution added, followed by fifty cc. of ninety-five per cent. alcohol. The whole was then boiled, filtered while hot, and washed with hot water containing thirty-five per cent. of alcohol.

	Wt. obtained.	Calculated.	Difference.
<i>Experiment 5.</i>	0.1200 gram.	0.1172	0.0028
" 6.	0.1230 "	0.1172	0.0058

*Experiments 7, 8, and 9.*—Thirty cc. of the sodium tungstate solution were diluted to seventy-five cc. with distilled water, and six cc. of the praseodymium chloride added, followed by twenty-five cc. of ninety-five per cent. alcohol. The whole was heated to 60° C. for half an hour, filtered while hot, and the precipitate washed with hot water containing twenty-five per cent. of alcohol.

	Wt. obtained.	Calculated.	Difference.
<i>Experiment 7.</i>	0.1733 gram.	0.1758	—0.0025
" 8.	0.1730 "	0.1758	—0.0028
" 9.	0.1724 "	0.1758	—0.0034

The precipitates after ignition showed traces of the blackish-brown praseodymium peroxide  $\text{Pr}_2\text{O}_5$ . The filtrate was tested with hydrogen sulphide, but gave no reaction for tungsten.

*Experiments 10, 11, 12, 13, and 14.*—Thirty cc. of the sodium tungstate solution were diluted to seventy-five cc. with distilled water, six cc. of the praseodymium chloride solution, and twenty-five cc. of alcohol added, and the whole heated for two hours at a temperature of 60° C. The precipitate was filtered off while the solution was hot, and was washed with 150 cc. hot water, containing twenty-five per cent. of alcohol.

	Wt. obtained.	Calculated.	Difference.
<i>Experiment 10.</i>	0.1715 gram.	0.1758	—0.0043
" 11.	0.1712 "	0.1758	—0.0046
" 12.	0.1713 "	0.1758	—0.0045
" 13.	0.1712 "	0.1758	—0.0046
" 14.	0.1713 "	0.1758	—0.0045

The ignited precipitates appeared to be homogeneous, no traces of  $\text{Pr}_2\text{O}_3$  showing.

The filtrates were all tested for tungsten with hydrogen sulphide, but no tungsten trisulphide was obtained. This test is not of much value, however, when alcohol is present, as that will prevent the precipitation of tungsten as sulphide to a great extent, so that small quantities will escape detection, unless the alcohol is removed by evaporation before the hydrogen sulphide is used. The precipitation of molybdenum does not seem to be hindered under the same conditions, the hydrogen sulphide bringing down minute traces in a solution containing thirty-three per cent. of alcohol.

As the error is constant, and the condition of precipitation the same for all the numbers of this series of experiments, it is probably due to the solubility of praseodymium tungstate in water containing alcohol.

#### ANALYSIS OF PRASEODYMIUM TUNGSTATE.

One-tenth of a gram of the salt was fused with three grams of equal parts of sodium carbonate and sulphur. The fused mass was taken up with water, the gray-green insoluble residue filtered off, and washed with cold water; the filtrate was acidified with hydrochloric acid, the precipitated tungsten trisulphide filtered off on a tared filter, and dried in the air-bath at  $100^\circ\text{C}$ . until a constant weight was obtained.

When allowance is made for the molybdic acid present in sodium tungstate the amount of sulphide obtained must be lower than that called for by theory for pure praseodymium tungstate. The praseodymium oxide should be slightly higher in amount.

To estimate the oxide the insoluble residue from the fusion was dissolved in hydrochloric acid, precipitated with oxalic acid and ammonium hydroxide, and ignited in a covered crucible as already described.

	Wt. obtained.	Calculated.	Theoretical.
$\text{Pr}_2\text{O}_3$	0.0334 gram.	0.0331	0.0325
$\text{WS}_3$	0.0806 "	0.0808	0.0814

These results leave no doubt but that the constitution of this salt is correctly represented by the formula  $\text{Pr}_2(\text{WO}_4)_3$ .

To determine the solubility of the salt, praseodymium chloride

was precipitated by sodium tungstate in aqueous solution; the precipitate with the solution was heated to 60°C. for two hours before filtering, and was washed with hot water until silver nitrate showed no trace of chlorine. The precipitate was dried in the air for a week, and then finely powdered. Portions of the salt were mixed with distilled water at different temperatures, about eighty cc. of water being taken for each portion, and then allowed to stand for two hours, the temperature being kept constant and the liquid frequently stirred. At the end of two hours they were filtered into weighed porcelain crucibles, evaporated to dryness, ignited, and weighed.

The results obtained are given below:

Temperature.	Wt. of solution.	$\text{Pr}_2(\text{WO}_4)_3$ .	Solubility.
20° C.	39.3817 grams.	0.0000	0:00000
20° C.	44.6541 "	0.0000	0:00000
75° C.	44.2312 "	0.0019	1:23300
75° C.	40.1484 "	0.0018	1:22300

#### SODIUM MOLYBDATE AND PRASEODYMIUM CHLORIDE.

The solution of sodium molybdate used contained 8.51 grams in one liter.

*Experiments 1-6.*—Twenty cc. of the sodium molybdate solution were diluted to seventy cc. with distilled water, then twelve cc. praseodymium chloride solution were added, followed by twenty-five cc. of alcohol. The whole was heated for two hours at a temperature of 65° C. The precipitate was then filtered off and washed with 150 cc. of hot water containing twenty-five per cent. of alcohol, ignited, and weighed.

	Wt. obtained.	Calculated.	Difference.
<i>Experiment 1.</i>	0.2093 gram.	0.2101	—0.0008
" 2.	0.2094 "	0.2101	—0.0007
" 3.	0.2096 "	0.2101	—0.0005
" 4.	0.2084 "	0.2101	—0.0017
" 5.	0.2084 "	0.2101	—0.0017
" 6.	0.2080 "	0.2101	—0.0021

The precipitates numbered 1, 2, and 3, all showed traces of praseodymium oxide  $\text{Pr}_2\text{O}_3$ ; the others seemed to be homogeneous.

The filtrates were all tested for molybdenum, with zinc, hydrochloric acid and potassium thiocyanate, but none was found. Alcohol does not interfere with the delicacy of this test.

The ignited salt was analyzed, the molybdic acid being determined by the Pechard method, while the praseodymium oxide was determined in the residue, after the molybdic acid was expelled, by the same method as had been pursued with the tungstate.

	Wt. obtained.	Calculated.
WO <sub>3</sub>	0.1135 gram.	0.1127
Pr <sub>2</sub> O <sub>3</sub>	0.0874 "	0.0873

The amount taken for analysis was two-tenths of a gram, and the results show the correct formula to be Pr<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub>, corresponding to that found for the tungstate.

The solubility of praseodymium molybdate was determined with the following results:

Temperature.	Wt. of solution.	Pr <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub> .	Solubility.
23° C.	71.4000 grams.	0.0011	1:65820
75° C.	69.8000 "	0.0010	1:69800

#### PRECIPITATION OF TUNGSTIC ACID WITH NEODYMIUM CHLORIDE.

The solution of sodium tungstate used contained five grams in one liter.

*Experiments 1 and 2.*—Twenty cc. of the sodium tungstate were diluted to 100 cc. with distilled water and five cc. of the neodymium chloride added, followed by twenty-five cc. of ninety-five per cent. alcohol. The whole was brought to boiling, filtered while hot, and the precipitate washed with hot water containing twenty-five per cent. of alcohol.

The filtrates were opalescent, and repeated filtrations failed to render them clear. The precipitates, after ignition, appeared to be homogeneous.

	Wt. obtained.	Calculated.	Difference.
<i>Experiment 1.</i>	0.1117 gram	0.1167	—0.0050
" 2.	0.1126 "	0.1167	—0.0041

*Experiments 3 and 4.*—Ten cc. of the sodium tungstate solution diluted to fifty cc. with distilled water, and three and one-half cc. of neodymium chloride solution added were heated to boiling, filtered while hot, and the precipitate washed with hot water.

	Wt. obtained.	Calculated.	Difference.
<i>Experiment 3.</i>	0.0595 gram.	0.0583	0.0012
" 4.	0.0573 "	0.0583	—0.0010

*Experiments 5-16.*—These experiments were duplicates of 3 and 4, excepting that the solutions were heated to 80° C. instead of to boiling. No alcohol was added, and the precipitates were washed with hot water. The precipitates showed traces of the brown peroxide,  $\text{Nd}_2\text{O}_3$ .

	Wt. obtained.	Calculated.	Difference.
<i>Experiment 5.</i>	0.0575 gram.	0.0583	—0.0008
" 6.	0.0575 "	0.0583	—0.0008
" 7.	0.0593 "	0.0583	+0.0001
" 8.	0.0600 "	0.0583	0.0017
" 9.	0.0585 "	0.0583	0.0002
" 10.	0.0586 "	0.0583	0.0003
" 11.	0.0590 "	0.0583	0.0007
" 12.	0.0585 "	0.0583	0.0002
" 13.	0.0585 "	0.0583	0.0002
" 14.	0.0581 "	0.0583	—0.0002
" 15.	0.0584 "	0.0583	0.0001
" 16.	0.0597 "	0.0583	0.0014

*Experiments 17 and 18.*—Thirty cc. of the sodium tungstate solution were diluted to seventy cc. with distilled water and six cc. of the neodymium chloride solution added, followed by twenty-five cc. of alcohol. The whole was heated to 70° C., filtered while hot, and the precipitate washed with hot water containing twenty-five per cent. of alcohol.

	Wt. obtained.	Calculated.	Difference.
<i>Experiment 17.</i>	0.1724 gram.	0.1749	—0.0025
" 18.	0.1745 "	0.1749	—0.0004

No. 18 showed slight traces of the peroxide  $\text{Nd}_2\text{O}_3$ .

*Experiments 19-21.*—These were prepared like the preceding solutions Nos. 17 and 18, but were heated to 60° C. instead of 70°.

The filtrates showed no trace of molybdenum when tested with zinc, hydrochloric acid, and potassium thiocyanate.

	Wt. obtained.	Calculated.	Difference.
<i>Experiment 19.</i>	0.1731 gram.	0.1749	—0.0018
" 20.	0.1727 "	0.1749	—0.0022
" 21.	0.1728 "	0.1749	—0.0021

A comparison of these results shows that the precipitation of tungstic acid by neodymium chloride is practically quantitative. Analyses of the salt made in the same manner as for praseodymium tungstate agreed closely with the theoretical requirements as regarded the neodymium oxide. The tungstic acid was inva-

riably too low, and the different results were too discordant; the tungstic acid, therefore, was determined by difference; the weight of neodymium oxide found was 0.0651 gram, the amount required by theory being 0.0652 gram. From this was deduced the formula  $\text{Nd}_2(\text{WO}_4)_3$  for the salt, which corresponds to the praseodymium tungstate.

The solubilities, determined as for the praseodymium salts, and under similar conditions were as follows:

Temperature.	Wt. of solution.	$\text{Nd}_2(\text{WO}_4)_3$ .	Solubility.
22° C.	42.1032 grams.	0.0008	1:52630
65° C.	41.7117 "	0.0007	1:59580
98° C.	39.6286 "	0.0006	1:66040

#### SODIUM MOLYBDATE AND NEODYMIUM CHLORIDE.

The solution of sodium molybdate used contained 5.1080 grams in one liter.

*Experiments 1-5.*—Twenty cc. of the sodium molybdate solution were diluted to seventy cc. with distilled water; seven cc. of the neodymium chloride solution were added, followed by twenty-five cc. of ninety-five per cent. alcohol. The whole was then heated to 65° C. for two hours, filtered hot, and the precipitate washed with 150 cc. of hot water containing twenty-five per cent. of alcohol.

The ignited precipitates showed no trace of the brown oxide  $\text{Nd}_2\text{O}_3$ , and the filtrates, when tested, gave no reaction for molybdenum.

	Wt. obtained.	Calculated.	Difference.
<i>Experiment 1.</i>	0.1260 gram.	0.1256	0.0004
" 2.	0.1259 "	0.1256	0.0003
" 3.	0.1260 "	0.1256	0.0004
" 4.	0.1259 "	0.1256	0.0003
" 5.	0.1258 "	0.1256	0.0002

An analysis of two-tenths of a gram of the salt made in the same way as the analysis of praseodymium molybdate gave the following results:

	Wt. obtained.	Calculated.	Difference.
$\text{Nd}_2\text{O}_3$	0.0863 gram.	0.0865	—0.0002
$\text{MoO}_3$	0.1134 "	0.1135	—0.0001

From these results the formula  $\text{Nd}_2(\text{MoO}_4)_3$  is deduced for neodymium molybdate.



The solubility determinations gave the following results :

Temperature.	Wt. of solution.	$\text{Nd}_2(\text{MoO}_4)_3$ .	Solubility.
28° C.	69.9311 grams.	0.0013	1:53790
75° C.	71.4279 "	0.0022	1:32466

A comparison of the results obtained shows that the precipitation of both tungstic and molybdic acids by neodymium salts is quantitative.

#### SODIUM TUNGSTATE AND LANTHANUM CHLORIDE.

The solution of sodium tungstate contained five grams in a liter.

*Experiments 1 and 2.*—Twenty cc. of sodium tungstate solution were diluted to seventy cc. with distilled water, and seven cc. of lanthanum chloride solution added, followed by twenty-five cc. of alcohol. The whole was heated for two hours at a temperature of 60° C., after which the precipitate was filtered off and washed with 150 cc. of hot water containing twenty-five per cent. of alcohol. The filtrate was clear and gave no reaction for tungsten with hydrogen sulphide. The ignited precipitates appeared to be homogeneous.

	Wt. obtained.	Calculated.	Difference.
<i>Experiment 1.</i>	0.1143 gram.	0.1160	—0.0017
" 2.	0.1143 "	0.1160	—0.0017

The tungstate before ignition was of a delicate blue, almost white, and after ignition the color deepened slightly. The color of the molybdate was almost the same as that of the tungstate.

#### ANALYSIS OF LANTHANUM TUNGSTATE.

The first analysis was made by fusing with sodium carbonate and sulphur, then taking up in water, and filtering off the sodium sulphotungstate formed, from the insoluble lanthanum oxide; then decomposing the filtrate with hydrochloric acid and estimating the tungsten from the tungsten trisulphide found.

The results obtained were very satisfactory so far as the lanthanum oxide was concerned, but no good results were obtained for the tungstic acid.

The amount of the salt taken for analysis was one-tenth of a gram.

	Wt. obtained.	Calculated.
$\text{La}_2\text{O}_3$	0.0326 gram.	0.0321
$\text{WS}_3$	0.0606 "	0.0822

The same difficulty was encountered here that was met with in the analysis of neodymium tungstate, and the cause was not apparent. A second analysis by a different method was made, the same amount of material being taken. The lanthanum tungstate was decomposed with aqua regia, evaporated to dryness with hydrochloric acid three times, and the separated tungsten trioxide filtered off and dissolved in ammonium hydroxide; the filtrate was rendered ammoniacal, the solution of the tungstic acid added to it, and hydrogen sulphide passed through it until the liquid was deep yellow in color. The liquid was acidified with hydrochloric acid, and before neutralization was complete the color changed to a bright green, becoming red when completely acidified. On rendering it ammoniacal again, the green color reappeared.

Hydrogen sulphide was passed through the solution again for an hour, hydrochloric acid added, and the solution warmed; it gradually became colorless, and a light brown precipitate of tungsten trisulphide settled down.

This was treated in the usual manner and dried at 100° to constant weight.

	Wt. obtained.	Calculated.
WS <sub>3</sub>	0.0640 gram.	0.0822

The filtrate was boiled until all the hydrogen sulphide was expelled, a few drops of nitric acid added, and then ammonium hydroxide; the precipitate of lanthanum hydroxide was evidently not pure, being yellow in color instead of white; it was filtered off, ignited, dissolved in aqua regia, evaporated to dryness, taken up with a little hydrochloric acid, followed by ammonia, and the treatment with hydrogen sulphide repeated. The yellow ammoniacal solution passed through the same color changes as before, when acidified. On heating, a dark red-brown precipitate formed which was filtered off, and washed with dilute hydrochloric acid, and then with alcohol. A great part of the precipitate dissolved in the alcohol to a dark red solution, the precipitate left on the filter-paper turning brown. This precipitate was ignited in a weighed porcelain crucible and evaporated with concentrated nitric acid until a constant weight was obtained. It had the appearance of tungstic acid.

Wt. obtained = 0.0073 gram.

The alcoholic filtrate was evaporated to dryness in a weighed porcelain crucible, and treated repeatedly with fuming nitric acid to oxidize any sulphur that might be present to sulphuric acid, which was removed by repeated evaporation with ammonium hydroxide. The substance remaining in the porcelain crucible had the appearance of molybdic acid. It was pale yellow in color, was readily soluble in ammonium hydroxide, and also dissolved in aqua regia to a bright yellow solution, separating out as a bright yellow powder on concentrating the solution. The yellow powder, when ignited, turned brown, but regained its color on cooling, finally, however, becoming lemon-yellow. When moistened with hydrochloric acid and heated, no blue color appeared. A faint orange-red solution was obtained by treatment with zinc, hydrochloric acid, and potassium thiocyanate. Heated on platinum foil with concentrated sulphuric acid no blue color was produced. The phosphorus bead was colorless, even after treating with tin on charcoal.

The weight obtained was 0.0076 gram. The second analysis gives the following results:

	Wt. obtained.	Calculated.
$\text{La}_2\text{O}_3$ .	0.0326	0.0321
$\text{WO}_3$ .	0.0613	0.0679
	0.0076	

This corresponds to the formula  $\text{La}_2(\text{WO}_4)_3$ , for lanthanum tungstate. The same salt was prepared by W. French Smith<sup>1</sup> by the precipitation of sodium tungstate with lanthanum salts.

The solubility of lanthanum tungstate in water was determined by the Victor Meyer method, the salt being prepared in the same way as the praseodymium tungstate.

Temperature.	Wt. of solution.	$\text{La}_2(\text{WO}_4)_3$ .	Solubility.
27° C.	60.5580 grams.	0.0007	1:86510
65° C.	42.4678 "	0.0010	1:42467

#### SODIUM MOLYBDATE AND LANTHANUM CHLORIDE.

The solution of sodium molybdate used contained 8.51 grams in one liter.

*Experiments 1-3.*—Twenty cc. sodium molybdate solution were diluted to seventy cc. with distilled water, seven cc. of lantha-

<sup>1</sup> "Ueber Didymium and Lanthanum." Inaugural Dissertation by W. French Smith. Göttingen, 1876.

num chloride solution added, followed by twenty-five cc. of ninety-five per cent. alcohol.

The precipitate, at first gelatinous, gradually became granular, and was filtered off, washed with 150 cc. hot water containing twenty-five per cent. of alcohol, ignited, and weighed.

	Wt. obtained.	Calculated.	Difference.
<i>Experiment 1.</i>	0.2063 gram.	0.2083	—0.0020
“ 2.	0.2061 “	0.2083	—0.0022
“ 3.	0.2063 “	0.2083	—0.0020

The filtrates were clear and gave no reaction for molybdenum when treated with potassium thiocyanate in the presence of zinc and hydrochloric acid.

The solubility of the salt obtained was determined under the following conditions:

Temperature.	Wt. of solution.	$\text{La}_2(\text{MoO}_4)_3$ .	Solubility.
25° C.	72.5500 grams.	0.0013	1:55800
85° C.	69.3474 “	0.0023	1:30150

#### ANALYSIS OF LANTHANUM MOLYBDATE.

The analysis was made in the same manner as with the other molybdates, the salt being decomposed in a current of dry hydrogen chloride gas. The molybdic acid was driven off very readily at first, but toward the close of the operation the full heat of the Bunsen burner was required. Two-tenths of a gram of the salt were taken for analysis, and results were as follows:

	Wt. obtained.	Calculated.
$\text{La}_2\text{O}_3$	0.0853	0.0856
$\text{MoO}_3$	0.1145	0.1144

From these results the formula  $\text{La}_2(\text{MoO}_4)_3$ , may be calculated for lanthanum molybdate.

Tests were now made with thorium chloride, potassium zirconium fluoride, and zirconium fluoride.

With thorium chloride no definite results could be obtained from either sodium molybdate or sodium tungstate; precipitates were formed with both salts even in quite dilute solutions, but they were slight in quantity, and ran through the filter in spite of every attempt to prevent it, whether filtered hot or cold. Neither alcohol nor ammonium salts made any difference in the behavior.

With the potassium zirconium fluoride no precipitate was obtained with either the sodium tungstate or molybdate.

With zirconium fluoride no results were obtained, the solutions remaining clear after standing several days.

Beyond these qualitative tests no work was done with the thorium or zirconium salts in connection with tungsten and molybdenum.

#### SUMMARY.

1. The tungstates and molybdates are precipitated quantitatively by nearly all the rare earths.
2. A separation of tungstic and molybdic acids is not possible through their combinations with the rare earths.
3. The non-precipitation of molybdic acid by uranyl solutions when tungstates are absent, and the almost complete precipitation of both when tungstic acid is also present is further evidence of the fact that we can scarcely hope to effect this separation by the method of precipitation.
4. The molybdates and tungstates of neodymium and praseodymium are new, and their constitution is correctly represented by the formula  $\text{Nd}_2(\text{MoO}_4)_3$ ,  $\text{Nd}_2(\text{WO}_4)_3$ , and  $\text{Pr}_2(\text{MoO}_4)_3$ ,  $\text{Pr}_2(\text{WO}_4)_3$ .
5. The solubility determinations indicate that tungstates and molybdates of the rare earths must be classed among the more difficultly soluble compounds.
6. Further research is required upon the methods to be followed in the separation of tungstic and molybdic acids from the oxides of the rare earths.

### A NEW TABLE FOR THE QUALITATIVE SEPARATION OF THE METALS OF THE IRON GROUP.

By C. L. HARE.

Received April 15, 1895.

**I**N the qualitative separation of metals of the iron group much trouble has been experienced with the methods in general use for the separation of cobalt and nickel.

The methods commonly used for the separation of iron, aluminum, and chromium are also unsatisfactory.

The following compilation and application of methods recently worked up greatly simplifies and shortens the process for the qualitative separation of the metals of this group.

In the separation of chromium from iron and aluminum advantage is taken of the well-known action of hydrogen peroxide on chromium compounds in presence of an alkali, the insoluble chromium compound being oxidized to soluble chromic acid. (Bauman *Ztschr. anal. chem.*, 1892 and others.)

The separation of nickel and cobalt, after the removal of manganese and zinc by hydrochloric acid, depends upon the solubility of nickel sulphide in a solution of sodium sulphide, the cobalt sulphide being insoluble in this reagent. (Villiers, *compt. rend.*, 119, 1263, and 120, 46.) The sulphides of the two metals are dissolved in aqua regia and the greater part of the acid expelled. The solution is diluted and a slight excess of tartaric acid is added to prevent precipitation of the two metals by sodium hydroxide, which is next added in great excess. Hydrogen sulphide is now passed through the hot solution till no further precipitation occurs. Cobalt sulphide is precipitated and the nickel sulphide is held in solution by the sodium sulphide. The presence of a trace of nickel is indicated by the deep brown or black color which it imparts to the solution. The nickel sulphide is precipitated from this solution by the addition of dilute hydrochloric acid.

The following is an outline of the treatment: To a solution of the metals of the iron group add ammonium chloride and ammonium hydroxide, warm, and filter. Boil the precipitated iron, aluminum, and chromium hydroxides with sodium hydroxide, filter, acidify the filtrate, and add ammonium hydroxide. A white precipitate indicates aluminum. Boil the residue of iron and chromium hydroxides with sodium hydroxide and a few cubic centimeters of hydrogen peroxide. Filter; a yellow solution indicates chromium. Acidify filtrate with acetic acid and add lead acetate. A yellow precipitate indicates chromium. Dissolve residue of iron hydroxide in hydrochloric acid and add potassium ferrocyanide. A blue precipitate indicates iron.

To the filtrate from iron, aluminum and chromium hydroxides add freshly prepared ammonium sulphide, heat, and filter. Wash the precipitate with cold dilute hydrochloric acid to dissolve manganese and zinc and treat the washings as usual for these two metals. Dissolve the residue of nickel and cobalt sul-

phides, left after washing with hydrochloric acid, in aqua regia, expel nearly all the acid, dilute, and add slight excess of tartaric acid, and then very great excess of sodium hydroxide. Boil and pass hydrogen sulphide through till no further precipitation occurs, filter immediately. Test the precipitate for cobalt by borax bead. The presence of nickel in the filtrate is indicated by its deep brown or black color. If nickel be absent the filtrate will be yellow or colorless.

If nickel be present add dilute hydrochloric acid to filtrate, filter, and test the precipitate for nickel by borax bead.

The ammonium sulphide should be prepared as recently as possible, as an excess of sulphur in solution causes the solution of a portion of the nickel sulphide.

## THE PROTEIDS OF BARLEY.<sup>1</sup>

BY THOMAS B. OSBORNE.

Received April 2, 1895.

THE proteids of barley have received little attention on the part of chemists. Mulder<sup>2</sup> states that this grain contains six per cent. of albumin and plant-gelatin; the latter was obtained by extracting barley-meal with hot alcohol, cooling the resulting solution and treating the deposited substance with ether. The composition of this body he gave as follows:

	1	2
Carbon .....	54.93	54.75
Hydrogen .....	7.11	6.99
Nitrogen .....	15.71	15.71
Sulphur .....	0.57	0.62
Oxygen.....	21.68	21.93
	100.00	100.00

v. Bibra<sup>3</sup> names albumin, plant-gelatin, and casein as constituents of barley but gives no particulars concerning these bodies further than that they all contain on the average 15.5 to 15.6 per cent. of nitrogen.

Kreusler made an investigation of the proteids of barley, the

<sup>1</sup> From the Report of the Connecticut Agricultural Experiment Station for 1894.

<sup>2</sup> Phys. Chem., I, 306-308.

<sup>3</sup> Die Getreidearten u. das Brod. Nürnberg, 1860, p. 304.

results of which are given by Ritthausen.<sup>1</sup> Kreusler employed coarsely ground meal and finely ground flour, the latter yielding purer preparations, the results being otherwise the same.

He states that the aqueous extract of the ground seed contains an albumin coagulated by boiling and of the following composition:

Carbon .....	52.86
Hydrogen .....	7.23
Nitrogen .....	15.75
Sulphur .....	1.18
Oxygen .....	22.98
	<hr/>
	100.00

The extract made with seventy-five per cent. alcohol contains, according to Kreusler, three proteids: gluten-casein, gluten-fibrin, and mucedin.

The gluten-casein separates on cooling the hot alcoholic extract, and when purified by boiling with dilute alcohol and fractionally precipitated from solution in acetic acid has the composition stated below.

1, is not corrected for ash and represents the first precipitation from a turbid solution.

2, is the second precipitation from a clear solution and is corrected for ash.

The cold alcoholic extract contains gluten-fibrin and mucedin.

The composition of these Kreusler gives as follows:

	Gluten-casein.		Gluten-fibrin.		Mucedin.	
	1.	2.	From meal.	From flour.	From meal.	From flour.
Carbon ....	53.84	53.25	55.23	54.55	53.19	53.97
Hydrogen ...	7.16	7.13	7.24	7.27	6.65	7.03
Nitrogen ....	16.63	....	15.49	15.70	16.14	16.98
Sulphur } ...	....	....	22.04	22.48	24.02	{ 0.68
Oxygen }						{ 21.34
						<hr/>
						100.00

These proteids were supposed to be the same as those similarly named and described by Ritthausen as occurring in the wheat kernel.

So far as the writer has been able to learn the preceding summary includes all that has been published hitherto in regard to the proteids of the barley kernel that is now worthy of notice.

<sup>1</sup> Die Eiweisskoerper, etc., Bonn, 1872, p. 103.



My preliminary examination of barley-meal showed that the seeds contain proteid matters soluble in water, in sodium chloride solutions, and in alcohol, and that after complete extraction with all these reagents there remains a considerable quantity of proteid which can be partly extracted by dilute potash solutions, but the greater part of which is insoluble in any reagent hitherto applied.

The material employed consisted of meal made from two-rowed barley and of a very white barley flour kindly furnished by the Health Food Co., of New York, both of which yielded proteids of the same composition and properties, the preparations derived from the flour, however, being less contaminated with coloring matter than those derived from the meal made from the entire grain, including the ground husk, which was so closely adherent, as to render its removal in the laboratory impossible.

#### PROTEIDS SOLUBLE IN WATER. LEUCOSIN. PROTEOSE.

As an aqueous extract of any seed, is in reality a dilute saline solution, owing to the salts extracted from the seed, and as the proteid matter soluble in alcohol dissolves to a slight extent in very dilute saline solutions, the proteids properly soluble in water were obtained by extracting the meal with sodium chloride solutions, dialyzing away the salts and filtering off the proteid that thereby precipitated. In this way the proteid matter, soluble in pure water, which had been extracted from the meal was obtained in solution by itself. Three kilos of barley, ground to a fine meal, were treated with nine liters of ten per cent. salt solution, applied in successive portions, the bran being removed by washing on a coarse cloth. The starch and other suspended matter was allowed to settle out and the extract was filtered clear. This solution was then saturated with ammonium sulphate and the precipitate produced, after filtering out, was treated with ten per cent. salt solution. The resulting liquid was filtered clear and dialyzed for five days. The globulin that separated in this process was collected on a filter, the solution was returned to the dialyzer for three days longer, and the very small additional amount of substance that separated was filtered out. The clear solution was then heated in a water-bath to 65°, the water of the bath not exceeding 70°. After an hour the coagulum was filtered

out, washed with warm water, alcohol, and ether, and dried over sulphuric acid. This preparation, 1, weighed 4.15 grams and when dried at 110° had the following composition:

COAGULATED BARLEY ALBUMIN, LEUCOSIN. *Preparation 1.*

Carbon .....	53.04
Hydrogen .....	6.78
Nitrogen .....	16.84
Sulphur.....	1.42
Oxygen .....	21.92
	<hr/>
	100.00
Ash .....	0.29

Another preparation was made by treating two kilos of barley meal with ten per cent. sodium chloride solution, squeezing out in a press and repeating the process on the residue. The filtered extract was saturated with ammonium sulphate, the precipitate dissolved in dilute salt solution, subjected to dialysis and, when freed from chlorides, filtered and heated to 65° in a water-bath of 70°. The coagulum produced was washed thoroughly with hot water, alcohol, and ether, and dried over sulphuric acid. This preparation, 2, weighed two and three-tenths grams and, when dried at 110°, had the following composition:

COAGULATED BARLEY ALBUMIN, LEUCOSIN. *Preparation 2.*

Carbon .....	52.67
Hydrogen.....	6.77
Nitrogen .....	16.41
Sulphur } .....	24.15
Oxygen }	
	<hr/>
	100.00
Ash.....	0.31

As this body separated slowly when its solutions were heated to 65° it was thought possible that more than one albumin was present which, if a fact, might be shown by analysis of preparations, precipitated in successive fractions.

Accordingly six kilos of barley-meal were extracted with ten per cent. salt solution and the clear filtered extract saturated with ammonium sulphate. The precipitate produced was dissolved in brine and the solution, after filtering clear, was dialyzed until all the the globulin had precipitated. It was then again filtered clear and in order to obtain a concentrated solution the filtrate

was saturated with ammonium sulphate, the precipitate formed was dissolved in water, and this solution was filtered clear and dialyzed. After six days only a very little more globulin had separated, which was filtered out, and a portion of the clear solution was tested carefully for its coagulation point. When slowly heated in a double water-bath it became faintly turbid at 39° and but very little more so at 49°. The turbidity then rapidly increased, flocks appearing at 56°. After heating at 56° for twenty minutes the solution was filtered and again heated. Turbidity occurred at 50° and flocks formed at 60°. After heating to 65° and holding at this temperature for some time the solution was filtered and again heated. Thereupon the turbidity took place at 70° and a very few flocks formed at 74°. The solution still had a just detectable acid reaction. The entire solution was then heated with great care to precisely 56° in a large water-bath, the temperature of which did not exceed 57°. After keeping at this temperature for an hour the coagulum was filtered out, washed with hot water, alcohol, and ether, and dried over sulphuric acid. This preparation, 3, weighed 0.36 gram and contained, when dried, without correction for ash, 16.48 per cent. of nitrogen.

The filtrate from preparation 3, was then heated to just 60° for three hours, and the second coagulum filtered off and treated as the first had been. This preparation, 4, weighed four-tenths gram and contained, without correcting for ash, 16.74 per cent. of nitrogen. Another part of this same extract, after freeing from globulin as above described, was dialyzed into alcohol for three days, whereby the solution was concentrated and the proteid partly precipitated. In order to separate the albumin from any proteose thrown down with it, the precipitate produced by alcohol-dialysis was digested with absolute alcohol for three days longer and then washed thoroughly with water. A considerable part of the albumin was thus rendered insoluble in water, and after being further washed with absolute alcohol and ether, was dried over sulphuric acid and found to weigh 0.51 gram. This preparation, 5, contained 16.30 per cent. of nitrogen without correcting for ash.

Another preparation of albumin was made in the same way, in

order to obtain a larger quantity for complete analysis. Six kilos of barley flour were mixed with twenty-eight liters of ten per cent. salt solution and seventeen liters of clear filtrate obtained, which was saturated with ammonium sulphate. The precipitate produced was dissolved as far as possible in ten per cent. salt solution, filtered clear, and in order to reduce the volume of the solution it was saturated with ammonium sulphate, the precipitate dissolved in 1000 cc. of water, and dialyzed until entirely free from globulin. The solution was then filtered and dialyzed into alcohol. After being concentrated, absolute alcohol was added and the precipitate filtered off, washed with absolute alcohol and ether, and dried over sulphuric acid. This preparation, 6, weighed four and one-tenth grams. It was then digested with water and the insoluble matter washed thoroughly with water, alcohol, and ether, dried over sulphuric acid, and had the following composition when dried at 110°:

COAGULATED BARLEY ALBUMIN, LEUCOSIN. *Preparation 6.*

Carbon .....	52.71
Hydrogen .....	6.78
Nitrogen .....	16.93
Sulphur.....	1.51
Oxygen .....	22.07
	<hr/>
	100.00
Ash .....	0.50

SUMMARY OF ANALYSES OF COAGULATED BARLEY ALBUMIN—LEUCOSIN.

	1.	2.	3. <sup>1</sup>	4. <sup>1</sup>	5. <sup>2</sup>	6. <sup>3</sup>	Average.
Carbon.....	53.04	52.67	....	....	..	52.71	52.81
Hydrogen..	6.78	6.77	....	....	....	6.78	6.78
Nitrogen...	16.84	16.41	16.48	16.74	16.30	16.93	16.62
Sulphur ...	1.42	24.15	....	....	....	1.51	1.47
Oxygen....	21.92					22.07	22.32
	<hr/>	<hr/>				<hr/>	<hr/>
	100.00	100.00				100.00	100.00

If this proteid be compared with the leucosin<sup>4</sup> obtained from the wheat and rye kernels, it will be seen that the three are almost identical in composition.

<sup>1</sup> Not corrected for ash.

<sup>2</sup> Not corrected for ash; coagulated by alcohol.

<sup>3</sup> Coagulated by alcohol.

<sup>4</sup> Report of the Connecticut Agricultural Experiment Station, 1893, p. 179.

LEUCOSIN.			
	Wheat.	Rye.	Barley.
Carbon.....	53.02	52.97	52.81
Hydrogen.....	6.84	6.79	6.78
Nitrogen.....	16.80	16.66	16.62
Sulphur.....	1.28	1.35	1.47
Oxygen.....	22.06	22.23	22.32
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

The aqueous extract of the barley kernel contains also a small quantity of one or more proteoses, but owing to the great difficulties encountered in attempting to separate these, no pure preparations have been obtained.

#### PROTEID SOLUBLE IN SODIUM CHLORIDE SOLUTION. EDESTIN.

The large amount of gum extracted from barley-meal by salt solution renders it very difficult to prepare the globulin in anything like a pure state. This difficulty is further increased by the readiness with which the globulin passes into the insoluble or albuminate condition and is thus lost for further purification. In only three cases was it possible to redissolve and reprecipitate this proteid in sufficient quantity for analysis. In all the extracts made, a considerable amount of globulin was precipitated by dialysis in the form of minute spheroids. So far as noticed, this globulin resembled, in all respects, that found in wheat and rye. It was readily and completely precipitated from salt solution by dialysis and also by adding acid. When dissolved in ten per cent. sodium chloride solution and heated, turbidity occurred at 90°, but no coagulum formed until the solution was boiled, and then only a small part of the dissolved substance separated.

Three kilos of barley-meal were extracted with ten per cent. salt solution, the filtered extract saturated with ammonium sulphate, and the resulting precipitate filtered out, dissolved in ten per cent. brine, and the insoluble matter removed by filtration after adding a *very* small quantity of two-tenths per cent. potash water in order to neutralize the slight acid reaction of the extract. The solution was then filtered clear and dialyzed for four days. The proteid separated in the form of small spheroids which were filtered out, washed with water, alcohol, and ether, and after drying over sulphuric acid found to weigh 4.02 grams. This

preparation was dissolved in ten per cent. salt solution and again submitted to dialysis. After the proteid had precipitated it was filtered out, washed with water, alcohol, and ether, and the final preparation, 7, when dried at 110°, had the following composition:

BARLEY GLOBULIN, EDESTIN, *Preparation 7.*

Carbon .....	51.43
Hydrogen .....	6.71
Nitrogen .....	18.14
Sulphur } .....	23.72
Oxygen } .....	
	<hr/>
	100.00
Ash .....	0.48

Again six kilos of barley flour were extracted with ten per cent. salt solution, the filtered extract saturated with ammonium sulphate, the resulting precipitate dissolved in salt solution and dialyzed. The precipitated globulin was again dissolved in ten per cent. salt solution and precipitated a second time by dialysis. One and nine-tenths grams of preparation 8 were obtained, having the following composition:

BARLEY GLOBULIN, EDESTIN, *Preparation 8.*

Carbon .....	50.82
Hydrogen .....	6.76
Nitrogen .....	18.16
Sulphur } .....	24.26
Oxygen } .....	
	<hr/>
	100.00
Ash .....	0.37

Another preparation was made in the same way, save that after dissolving the ammonium sulphate precipitate in salt solution, the proteids were again precipitated by saturation with ammonium sulphate and redissolved in brine, thus yielding a solution of smaller volume which was then dialyzed. After five days' dialysis, the chlorides having been removed, the precipitated globulin was treated in the usual manner and found to weigh 1.85 grams. This preparation, 9, had the following composition:

BARLEY GLOBULIN, EDESTIN, *Preparation 9.*

Carbon .....	50.40
Hydrogen .....	6.48
Nitrogen .....	18.00
Sulphur } .....	25.12
Oxygen } .....	
	100.00
Ash .....	0.44

The foregoing analyses, although not showing the agreement to be desired, are on the whole sufficiently alike to warrant their publication, and for the sake of comparison they are here tabulated.

## BARLEY GLOBULIN, EDESTIN.

	7.	8.	9.	Average.
Carbon.....	51.43	50.82	50.40	50.88
Hydrogen .....	6.71	6.76	6.48	6.65
Nitrogen .....	18.14	18.16	18.00	18.10
Sulphur } .....	23.72	24.26	25.12	24.37
Oxygen } .....				
	100.00	100.00	100.00	100.00

In view of the close resemblance in properties and similarity in composition it is the writer's opinion that this globulin is the same as that found in a large number of other seeds and previously described under the name edestin.<sup>1</sup> The following table affords a comparison of the composition of this proteid from its different sources.

## EDESTIN.

	Wheat.	Maize.	Hemp-seed.	Castor-bean.	Squash-seed.	Flax-seed.	Cotton-seed.	Rye.	Barley.
C....	51.03	51.71	51.28	51.31	51.66	51.48	51.71	51.19	50.88
H ...	6.85	6.85	6.84	6.97	6.89	6.94	6.86	6.74	6.65
N....	18.39	18.12	18.84	18.75	18.51	18.60	18.64	18.19	18.10
S ....	0.69	0.86	0.87	0.76	0.88	0.81	0.62	23.88	24.37
O ....	23.04	22.46	22.17	22.21	22.06	22.17	22.17		
	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

On comparing the above analyses it will be seen that the preparations obtained from the cereals show the greatest deviation from the average of these figures. This is unquestionably due to the fact that in these seeds this substance is present in small

<sup>1</sup> Report Connecticut Agricultural Experiment Station, 1893, pp. 179 and 216.

quantity and is associated with other bodies so that it has been impossible to prepare it from them in a state of perfect purity.

PROTEID SOLUBLE IN DILUTE ALCOHOL. HORDEIN.

After extracting 500 grams of barley-meal with brine the residue was treated with alcohol added in sufficient quantity to form with the water retained by the meal, an alcohol of approximately seventy-five per cent. After digesting a short time, the meal was squeezed out and again treated with seventy-five per. cent. alcohol, and pressed out. The united alcoholic extracts were then filtered clear, concentrated to small volume on a water-bath cooled, and the proteid thus separated washed thoroughly by kneading with distilled water. The separated substance now presented every appearance of gliadin, the proteid similarly obtained from wheat and rye. It was dissolved in a little dilute alcohol in which it was very readily soluble with the exception of a slight residue of coagulated proteid which rendered filtration extremely difficult. The solution was then precipitated by pouring into absolute alcohol and the precipitate digested with absolute alcohol, rubbed to a powder while still moist with alcohol, and treated with ether. When dried over sulphuric acid this preparation, 10, weighed 4.54 grams, and when dried at 110° gave on analysis the following results:

BARLEY PROTEID, *Preparation 10.*

	I.	II.	Average.
Carbon.....	53.83	53.93	53.88
Hydrogen.....	6.72	6.92	6.82
Nitrogen.....	17.32	....	17.32
Sulphur } .....	....	....	21.98
Oxygen } .....	....	....	
			<hr/> 100.00
Ash .....			0.22

Another extract was made by treating 500 grams of barley-meal with three liters of alcohol of nine-tenths specific gravity applied directly to the freshly ground meal. The extract, which had a red-brown color, was squeezed out in a press and concentrated to about one-eighth of its volume. After standing over night the mother-liquor was poured off from the proteid which had separated in a firm mass on the bottom of the dish.



This was then dissolved in dilute alcohol and precipitated by pouring into absolute alcohol. The resulting precipitate was washed with absolute alcohol, digested with ether, dried over sulphuric acid, and found to weigh 12.3 grams. This preparation, 11, when dried at 110°, had the following composition:

BARLEY PROTEID, *Preparation 11.*

Carbon .....	53.78
Hydrogen .....	6.51
Nitrogen .....	17.27
Sulphur.....	0.95
Oxygen .....	21.49
	<hr/>
	100.00
Ash .....	0.19

The remainder of preparation 11 was then dissolved in dilute alcohol and, after filtering clear, poured into distilled water and precipitated by adding a few drops of sodium chloride solution. This substance was again dissolved in dilute alcohol and precipitated by pouring into absolute alcohol. After treating with ether and drying at 110°, this preparation, 12, was analyzed with the following results:

BARLEY PROTEID, *Preparation 12.*

Carbon .....	53.78
Hydrogen .....	6.82
Nitrogen .....	17.16
Sulphur .....	0.93
Oxygen .....	21.31
	<hr/>
	100.00
Ash .....	0.86

Three kilos of barley-meal were treated with ten per cent. salt solution and washed on a coarse cloth until only the bran and larger particles of meal remained. This residue was then extracted with alcohol of nine-tenths specific gravity, yielding a deep red solution, which was filtered through animal charcoal; but only a part of the coloring-matter was removed. The clear solution was next concentrated on a water-bath, poured into absolute alcohol, and the resulting precipitate digested with absolute alcohol and treated with ether, giving preparation 13, weighing thirty grams and, when dry, having the following composition:

BARLEY PROTEID, *Preparation 13.*

	I.	II.	Average.
Carbon.....	53.80	53.70	53.75
Hydrogen.....	....	6.78	6.78
Nitrogen.....	17.48	17.33	17.41
Sulphur .....	0.93	....	0.93
Oxygen .....	....	....	21.13
			<hr/> 100.00
Ash .....			0.25

A portion of the solution from which preparation 13 had been obtained was precipitated separately by pouring into strong alcohol and adding a few drops of salt solution. The precipitate was treated in the usual manner and gave a preparation, 14, containing much less coloring-matter than the preceding and having the following composition :

BARLEY PROTEID, *Preparation 14.*

Carbon .....	54.32
Hydrogen .....	6.74
Nitrogen .....	17.13
Sulphur } .....	21.81
Oxygen }	
	<hr/> 100.00
Ash .....	1.43

The starchy portion of the barley-meal which had been washed through the cloth, as described, was thoroughly extracted with salt solution and then with dilute alcohol, the extraction being repeated until the proteid was completely removed. The united extracts were filtered and concentrated to two-thirds of their volume by distillation when the solution was poured into a dish and the evaporation continued. The proteid separated as a skin on the surface of the liquid and as a solid mass on the bottom of the dish. When reduced to about one-half the volume of the original liquid the hot mother-liquor was decanted from the separated proteid which formed a tough mass of a pink color. This was washed with water and redissolved in dilute alcohol, giving a deep red solution which was poured into absolute alcohol and the mass of substance that separated was cut up with scissors into small pieces and digested with absolute

alcohol and with ether. When dried over sulphuric acid this preparation, 15, was pinkish in color and weighed thirty grams. Dried at 110° and analyzed the following results were obtained :

BARLEY PROTEID, *Preparation 15.*

Carbon .....	54.00
Hydrogen .....	6.72
Nitrogen .....	17.49
Sulphur } .....	21.79
Oxygen } .....	
	<hr/>
	100.00
Ash .....	0.95

The mother-liquor decanted from preparation 15, was still further concentrated and allowed to cool over night. Only a little substance separated which, however, was washed with water, redissolved in dilute alcohol, and precipitated by pouring into much distilled water to which a little salt had been added. On standing about thirty-six hours the milky solution cleared and the proteid was found in a transparent layer at the bottom of the vessel. After treating with absolute alcohol and ether and drying over sulphuric acid, preparation 16 was obtained weighing seven grams and having when dried, the following composition :

BARLEY PROTEID, *Preparation 16.*

Carbon .....	53.90
Hydrogen .....	6.63
Nitrogen .....	17.08
Oxygen } .....	22.39
Sulphur } .....	
	<hr/>
	100.00
Ash .....	0.23

As this proteid resembled gliadin so closely in its physical and chemical properties it seemed important to subject it to very thorough fractional precipitation in order to determine whether it was a mixture of gliadin with another body or a new, distinct proteid. Another extract was made by treating three kilos of freshly ground barley-meal with ten per cent. salt solution, squeezing out in a press, and treating the residue again in the same way. The meal residue was then mixed with alcohol in

quantity sufficient to make, with the water retained by the meal, an alcohol of about forty per cent. After squeezing out the liquid, alcohol was again added to the residual meal sufficient to increase the strength of the solvent to seventy-five per cent. After digesting for some time the extract was squeezed out and found less colored than the first dilute alcohol extract. This second extract was concentrated by distillation to small volume and cooled giving a deposit of proteid much whiter than any previously made. The mother-liquor from this precipitate was poured into absolute alcohol and a second precipitate obtained. The two precipitates, when united, dehydrated in the usual way, treated with ether, and dried over sulphuric acid, weighed twenty-two grams. Dried at  $110^{\circ}$  this substance had the following composition:

*BARLEY PROTEID, Preparation 17.*

Carbon .....	54.30
Hydrogen .....	6.67
Nitrogen .....	17.47
Sulphur .....	0.84
Oxygen .....	20.72
	<hr/>
	100.00

About eighteen grams of this preparation were dissolved in alcohol of 0.9 specific gravity and absolute alcohol was added until a considerable precipitate resulted, when the mixture was heated on a water-bath until the precipitate dissolved. The solution was then cooled and after standing some time the mother-liquor was decanted from the separated substance. This precipitate was marked I. The solution decanted from I, was further treated with absolute alcohol and a second precipitate II, obtained in the same way. The mother-liquor from II was mixed with a large quantity of absolute alcohol and, as the proteid did not separate, a few drops of salt solution were added and the resulting precipitate III filtered off and treated with absolute alcohol and ether in the usual manner.

In the first place, precipitate I was dissolved in a small quantity of seventy-five per cent. alcohol and absolute alcohol was added until the precipitate began to reappear. The whole was heated until the precipitate again dissolved whereupon the solu-

tion was cooled. The substance which separated settled out leaving the solution milky. The mother-liquor was decanted from the small amount of deeply colored proteid which adhered to the bottom of the beaker, and this deposit was dissolved in a little seventy-five per cent. alcohol, treated with absolute alcohol, and the opalescent solution so produced mixed with a little ether. This gave a very small precipitate, almost black in color and very sticky. The solution decanted from this small deposit was treated with a drop of potassium acetate solution and the resulting precipitate, after washing with absolute alcohol and ether, dried over sulphuric acid. It formed a light pink powder, preparation 18, weighing 0.65 gram and when dry contained, ash-free, 16.60 per cent. of nitrogen. Its ash content was 1.04 per cent. The mother-liquor, decanted from the first precipitation of 18, was treated with a drop of potassium acetate solution and the precipitate produced allowed to settle. After standing, the substance settled out and adhered to the bottom of the beaker in a solid mass, from which the clear supernatant solution was decanted. This solution after treatment with absolute alcohol yielded a precipitate which, washed with absolute alcohol and ether, and dried, formed preparation 19, weighing 1.79 grams and having the following composition:

*BARLEY PROTEID, Preparation 19.*

Carbon .....	53.85
Hydrogen .....	6.69
Nitrogen .....	17.22
Sulphur ) .....	22.24
Oxygen ) .....	
	100.00
Ash .....	0.40

The substance deposited after the addition of potassium acetate to the solution from which 19 was derived, was dissolved in seventy-five per cent. alcohol, absolute alcohol added to the solution, and the resulting precipitate dissolved by heating. On cooling, a part of the proteid separated and after this had settled, the liquid was decanted and mixed with absolute alcohol, and on treating the precipitate in the usual manner preparation 20 was obtained, which when dried weighed 1.18 gram and gave the following results on analysis:

BARLEY PROTEID. *Preparation 20.*

Carbon .....	54.33
Hydrogen .....	6.81
Nitrogen .....	16.93
Sulphur } .....	21.93
Oxygen }	
	100.00
Ash.....	0.58

The substance deposited by cooling the solution from which 20 was obtained was only partly soluble in dilute alcohol. It was accordingly treated with seventy-five per cent. alcohol and allow to stand until the insoluble matter had settled out. The clear liquid was then decanted and completely precipitated with absolute alcohol. The separated substance was washed with absolute alcohol and ether and when dry weighed 0.81 gram. This preparation, 21, contained, ash-free, 16.65 per cent. of nitrogen and 0.32 per cent. of ash. The insoluble matter just described, after washing by decantation with seventy-five per cent. alcohol, was treated in the usual manner and yielded preparation 22, weighing 1.56 grams and having the following composition :

BARLEY PROTEID. *Preparation 22.*

Carbon .....	53.91
Hydrogen .....	6.77
Nitrogen .....	17.00
Sulphur } .....	22.32
Oxygen }	
	100.00
Ash.....	0.71

Precipitate II was dissolved in a little seventy-five per cent. alcohol and the solution mixed with absolute alcohol. The resulting precipitate (*a*) was dissolved by heating and the solution cooled, whereupon a part (*b*) of the proteid was precipitated. The supernatant solution was poured off, mixed with absolute alcohol, and this precipitate (*c*) which contained all the proteid remaining was dehydrated with absolute alcohol and washed with ether, giving preparation 23, weighing two and

two-tenths grams and having, when dry, the following composition :

BARLEY PROTEID. *Preparation 23.*

	I.	II.	Average.
Carbon.....	54.63	54.68	54.65
Hydrogen.....	6.62	6.50	6.56
Nitrogen .....	17.16	.....	17.16
Sulphur } .....	.....	.....	21.63
Oxygen } .....	.....	.....	.....
			100.00
Ash.....			0.32

The substance (*b*), deposited on cooling the solution as above described, was dissolved in seventy-five per cent. alcohol and partly precipitated by adding absolute alcohol. After redissolving the precipitate by the application of heat, the solution was cooled and allowed to stand some time to deposit the precipitate which formed. The liquid was then decanted and the separated substance treated with absolute alcohol and ether, yielding preparation 24, weighing 3.11 grams and having the following composition after drying at 110°.

BARLEY PROTEID. *Preparation 24.*

Carbon .....	54.27
Hydrogen.....	6.67
Nitrogen .....	17.39
Sulphur } .....	21.67
Oxygen } .....	.....
	100.00
Ash.....	0.32

To the solution from which 24 separated, absolute alcohol was added in considerable quantity and the proteid thus thrown down was dehydrated with absolute alcohol and washed with ether. When dried this preparation, 25, weighed 0.87 gram and, without correction for ash, contained 17.28 per cent. of nitrogen.

Precipitate III was treated with absolute alcohol and with ether, and dried over sulphuric acid. It weighed 1.63 grams and its composition after complete drying was :

BARLEY PROTEID. *Preparation 26.*

Carbon .....	53.39
Hydrogen.....	7.02
Nitrogen .....	17.49
Sulphur } .....	22.10
Oxygen } .....	
	100.00
Ash.....	0.59

If these figures are compared it will be seen that no fractional separation has been effected, the variations in the results being no greater than in the preparations previously described. Preparation 18 is low in nitrogen, but this is doubtless due to its containing nearly all the impurities precipitable from the solution. Preparation 21 is also low in nitrogen but this was the most colored of all the preparations and as it was also small in quantity the accuracy of the analysis could not be confirmed. Excluding these two preparations the results agree fairly as shown by the following table :

## SUMMARY OF THE PRECEDING FRACTIONAL PRECIPITATES.

	19.	20.	22.	23.	24.	25.	26.	Original substance 17.
Carbon ...	53.85	54.33	53.91	54.65	54.27	....	53.39	54.30
Hydrogen	6.69	6.81	6.77	6.56	6.67	....	7.02	6.67
Nitrogen..	17.22	16.93	17.00	17.16	17.39	17.28	17.49	17.47
Sulphur } .....	22.22	21.93	22.32	21.63	21.67	....	22.10	21.56
Oxygen } .....								
	100.00	100.00	100.00	100.00	100.00		100.00	100.00
Weight ...	1.79	1.18	1.56	2.2	3.11	0.87	1.63	18.00

As all the preceding preparations were made by extracting barley-meal which contained a large quantity of bran, they were much contaminated with coloring-matter.

In order to obtain products free from color 880 grams of fine ground "pearled barley" (a commercial preparation of barley made by rubbing off the outer coat of the grain), were treated with salt solution, and after squeezing out the excess of liquid, the residue was digested with seventy-five per cent. alcohol. The extract was then filtered, concentrated to small volume, cooled, and the mother-liquor decanted from the separated proteid. This was then dissolved in dilute alcohol, the solution



poured into distilled water, and the proteid thrown down by adding a little salt. The precipitate was again dissolved in a small amount of dilute alcohol and reprecipitated by pouring into absolute alcohol, digested with absolute alcohol for some time, then with ether, dried over sulphuric acid, and found to weigh eight grams. This preparation, 27, was pure white and had the following composition when thoroughly dried :

BARLEY PROTEID. <i>Preparation 27.</i>	
Carbon .....	54.37
Hydrogen .....	6.81
Nitrogen .....	17.33
Sulphur .....	0.88
Oxygen.....	20.61
	<hr/>
	* 100.00
Ash.....	0.48

Another preparation was made by extracting six kilos of barley flour with salt solution and then treating the residue with alcohol added in sufficient quantity to make with the water of the brine, which still adhered to the meal, as nearly as possible seventy-five per cent. alcohol. After standing over night the extract was filtered off, concentrated to about one-third its original volume, and cooled slightly. The proteid that now separated out from the hot solution was removed from the liquid, rinsed with water, dissolved in a very little dilute alcohol to a thick syrup, and reprecipitated by pouring into absolute alcohol. The substance was then cut up into small pieces and digested with absolute alcohol and also with ether. When dried over sulphuric acid seventy-eight grams of a pure white preparation were obtained. Twenty-five grams of this were then dissolved in seventy-five per cent. alcohol and the clear solution poured into a large volume of distilled water. A part of the substance separated, leaving the liquid milky. The milky solution was decanted from the separated substance and the latter was washed with water in which some of it dissolved. The turbid liquid and washings were united and precipitated with a little salt solution. After standing over night the proteid separated as a transparent viscid liquid on the bottom of the vessel in the same way as gliadin does under similar conditions. After decanting the supernatant

liquid the deposit was dissolved in dilute alcohol and precipitated by pouring its solution into absolute alcohol. The separated proteid was then digested with absolute alcohol and with ether, and dried over sulphuric acid. A pure white preparation, 28, resulted, which when dried at 110° had the following composition :

BARLEY PROTEID. *Preparation 28.*

Carbon .....	54.02
Hydrogen.....	6.79
Nitrogen .....	17.38
Sulphur .....	0.84
Oxygen.....	20.97
	<hr/>
	100.00
Ash.....	1.00

The mass which separated on pouring the alcoholic solution into water, as above described, was dissolved in seventy-five per cent. alcohol and, as it contained a little insoluble proteid which rendered filtration impossible, the solution was allowed to stand over night. The clear supernatant solution was then poured off and concentrated to about one-third of its volume and cooled. The proteid which separated was again dissolved in dilute alcohol and precipitated by pouring into absolute alcohol. After thorough dehydration with absolute alcohol and digestion with ether, the substance was dried over sulphuric acid and yielded preparation 29, which was white in color and weighed 5.46 grams. This substance, when dried, had the following composition :

BARLEY PROTEID. *Preparation 29.*

	I.	II.	Average.
Carbon.....	54.48	54.54	54.51
Hydrogen.....	6.70	6.79	6.75
Nitrogen .....	17.22	17.18	17.20
Sulphur } .....	21.60	21.49	21.54
Oxygen			
	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00
Ash.....			0.32

Another preparation was made without heating, by pouring a part of the original extract from which preparations 28 and 29 were derived into a large amount of distilled water and allowing

the separated substance to deposit. After some time this settled and the supernatant liquid was poured off, the precipitate washed with water, dissolved in cold dilute alcohol, and the solution poured into absolute alcohol. The precipitate produced was digested with absolute alcohol and then with ether and dried over sulphuric acid, yielding a pure white preparation having, when dry, the following composition :

BARLEY PROTEID. <i>Preparation 30.</i>	
Carbon.....	54.23
Hydrogen.....	6.83
Nitrogen .....	17.27
Sulphur .....	0.75
Oxygen.....	20.92
	<hr/>
	100.00
Ash.....	0.17

In order to obtain a larger quantity of a colorless preparation, five kilos of barley flour were treated with 10.5 liters of seventy-five per cent. alcohol, and after standing some time the extract was filtered off and six liters of clear solution obtained. This was then concentrated to one-third its volume and rapidly cooled. The proteid separated as a bulky plastic mass, which, after decanting the mother-liquor, was macerated with about 500 cc. of distilled water, the washings were poured off, and the mass of proteid dissolved in 500 cc. of seventy-five per cent. alcohol, yielding a solution of a pale yellowish brown tint. This solution was poured in a thin stream into a quantity of distilled water, and the separated proteid, after removal from the liquid, was again dissolved in seventy-five per cent. alcohol, and the perfectly clear solution poured in a small stream into a large quantity of absolute alcohol. As the soluble salts had been almost completely removed the proteid did not separate even after admixture of 800 cc. of absolute ether. Three or four cc. of salt solution were therefore added to the milky liquid, and an immediate precipitate resulted which rapidly settled, leaving the solution clear and free from proteid. This mixture of absolute alcohol and ether retained all the fat present in the proteid before precipitation, and also some coloring-matter, the liquid being yellow. The solution was decanted and the voluminous precipitate treated with successive portions of absolute alcohol, and

obtained as a snow-white granular substance, weighing, when dried over sulphuric acid, ninety-three grams. This preparation, 31, had the following composition when dried at 110°:

BARLEY PROTEID. *Preparation 31.*

	I.	II.	Average.
Carbon.....	54.18	54.31	54.25
Hydrogen.....	6.98	6.65	6.82
Nitrogen.....	17.20	17.30	17.25
Sulphur.....	0.84	....	0.84
Oxygen.....	....	....	20.84
			100.00
Ash .....			0.09

In order to make certain that this proteid, which so closely resembled gliadin in every respect but composition, was not that substance contaminated with fat, a portion of this preparation was ground to a very fine powder and washed for a long time with hot ether in an extraction apparatus. Only a trace of substance was removed by this treatment, and the proteid after drying, had the same composition as before, as the following figures show:

BARLEY PROTEID. *Preparation 32.*

Carbon .....	54.20
Hydrogen.....	6.58
Nitrogen.....	17.07
Sulphur .....	0.91
Oxygen.....	21.24
	100.00
Ash.....	0.25

Another portion of 31 was dissolved in two-tenths per cent. potash water, yielding a clear solution, which was precipitated by neutralization with two-tenths per cent. hydrochloric acid. The precipitate was washed with water, dehydrated with absolute alcohol, washed with ether, and analyzed with the following results:

BARLEY PROTEID. *Preparation 33.*

Carbon .....	54.21
Hydrogen.....	6.87
Nitrogen.....	17.12
Sulphur .....	0.76
Oxygen.....	21.04
	100.00
Ash.....	0.25

Preparation 31 was then subjected to fractional precipitation in order to make sure that it was not a mixture of two or more

proteids. Twenty-five grams were dissolved in 300 cc. of alcohol of 0.865 sp. gr. by heating on a water-bath, and the solution was quickly cooled. After adding a few drops of ten per cent. salt solution the most of the proteid separated in a coherent mass, leaving the liquid clear. After decantation, the residue was treated in the same way again, the decanted solutions being united. The residue was again dissolved and absolute alcohol added to the hot solution until a considerable precipitate resulted, when it was heated until clear and then cooled. A few drops of salt solution were then added and the proteid precipitated, leaving the solution slightly milky. This liquid was joined to the two solutions from which the proteid had been previously separated, and a little more salt solution added to the mixture, thereby precipitating the remainder of the dissolved proteid. After decanting the liquid from the separated substance the latter was treated with absolute alcohol and gave preparation 34, representing the fraction soluble in the strongest alcohol and having, when dry, the following composition:

BARLEY PROTEID. *Preparation 34.*

Carbon .....	54.32
Hydrogen.....	6.78
Nitrogen .....	17.02
Sulphur .....	0.94
Oxygen.....	20.94
	<hr/>
	100.00
Ash.....	0.21

The proteid, which had been precipitated during the preparation of this substance as just described, was dissolved in alcohol of 0.865 sp. gr., and the solution cooled rapidly by immersing in cold water. When a part of the substance had separated the solution was decanted and the separated substance treated with absolute alcohol. Preparation 35 was thus obtained, which gave the following figures on analysis:

BARLEY PROTEID. *Preparation 35.*

Carbon .....	54.47
Hydrogen.....	7.01
Nitrogen .....	17.15
Sulphur .....	0.74
Oxygen.....	20.63
	<hr/>
	100.00
Ash.....	0.43

The above preparation represented the portion least soluble in strong alcohol. The solution decanted from this preparation was precipitated with absolute alcohol and a few drops of salt solution, and the resulting precipitate, after the usual treatment, yielded preparation 36, having the following composition:

BARLEY PROTEID. *Preparation 36.*

Carbon .....	54.37
Hydrogen.....	6.81
Nitrogen .....	17.30
Sulphur .....	0.84
Oxygen.....	20.68
	<hr/>
	100.00
Ash.....	0.38

The following table includes all analyses of the preparations which were free from coloring-matter. .

HORDEIN. BARLEY PROTEID SOLUBLE IN DILUTE ALCOHOL.

	27.	28.	29.	30.	31.	32.
Carbon .....	54.37	54.02	54.51	54.23	54.25	54.20
Hydrogen.....	6.81	6.79	6.75	6.83	6.82	6.58
Nitrogen .....	17.33	17.38	17.20	17.27	17.25	17.07
Sulphur.....	0.88	0.84	21.54	0.75	0.84	0.91
Oxygen.....	20.61	20.97		20.92	20.84	21.24
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00	100.00	100.00	100.00
		33.	34.	35.	36.	Average.
Carbon.....		54.21	54.32	54.47	54.37	54.29
Hydrogen .....		6.87	6.78	7.01	6.81	6.80
Nitrogen .....		17.12	17.02	17.15	17.30	17.21
Sulphur .....		0.76	0.94	0.74	0.84	0.83
Oxygen .....		21.04	20.94	20.63	20.68	20.87
		<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
		100.00	100.00	100.00	100.00	100.00

This body differs essentially from all the well-defined plant proteids now known. As it appears to be characteristic of barley, I propose to adopt for it the latterly disused name *hordein*, which was first applied about 1870 by Proust<sup>1</sup> and ten years later by Hermbstädt<sup>2</sup> to certain products of their attempts to isolate the proximate principles of this cereal.

Hordein appears to have been obtained nearly pure from bar-

<sup>1</sup> Ann. chim. phys., 5, 337.

<sup>2</sup> J. tech. Chem., 12, 46.

ley flour by Kreusler, as shown by the following comparison of his analysis with the average above given.

## BARLEY PROTEID SOLUBLE IN DILUTE ALCOHOL.

	Kreusler.	Osborne.
Carbon....	53.97	54.29
Hydrogen.....	7.03	6.80
Nitrogen .....	16.98	17.21
Sulphur .....	0.68	0.83
Oxygen.....	21.34	20.87
	<hr/> 100.00	<hr/> 100.00

Ritthausen regarded this proteid as identical with the mucedin believed by him to occur in wheat and rye, but which, as my investigations prove, does not exist in those grains.

Toward water my different preparations of hordein behave somewhat differently. Preparations dried over sulphuric acid and still retaining a little alcohol dissolve in cold water to a greater or less extent according to the amount of alcohol present. When dried completely at  $110^{\circ}$ , so that all the alcohol is removed, very little hordein dissolves in cold water and slightly more on raising the temperature. Solutions thus made with hot water do not precipitate on cooling or coagulate on boiling although they give no inconsiderable precipitates on adding salt. A large number of preparations of this proteid and of wheat gliadin were thus tested and compared under similar conditions. The gliadin showed variations in solubility in the same way as the barley proteids, but throughout was much more soluble than the latter, yielding solutions with warm water which were precipitated by cooling. As drying at  $110^{\circ}$  tends to render more or less of these proteids insoluble in seventy-five per cent. alcohol it is not possible to say definitely whether the difference was due to original difference in properties of the two proteids tested or to the drying. It is the opinion of the writer that the hordein of barley is decidedly less soluble in water than the gliadin of wheat.

Toward alcohol the hordein behaves, so far as could be detected, exactly like gliadin. In very dilute acids and alkalies it is readily soluble and is precipitated by neutralization. Dissolved in concentrated hydrochloric acid a beautiful crimson color is produced similar to that given by gliadin under like

conditions. With a warm mixture of equal volumes of water and concentrated sulphuric acid a red color is given by hordein, not a purple red as by gliadin.

The most marked difference between hordein and gliadin is in composition, since hordein contains one and a half per cent. more carbon, one and a half per cent. less nitrogen, and three-tenths per cent. less sulphur than gliadin.

In the extraction last described 5000 grams of barley flour were treated with 10.5 liters of alcohol, and the extract obtained measured six liters, which was equivalent to 57.1 per cent. of the whole solution employed. If we assume, as is very nearly true, that this was equal to a complete extraction of 57.1 per cent. of the flour, the proteid obtained was equivalent to all the alcohol soluble proteid contained in 2855 grams of flour. In addition to the ninety-three grams of proteid above described, there was obtained a further quantity weighing, when thoroughly dried over sulphuric acid, 17.5 grams, thus making in all 110.5 grams. This quantity is 3.87 per cent. of the 2855 grams extracted. In order to confirm these figures 500 grams of barley flour were extracted with two liters of hot seventy-five per cent. alcohol, squeezed out in a press and the residual meal treated again in the same way with another liter of alcohol and the united extracts filtered clear and concentrated by evaporation. All the proteid contained in the solution separated on cooling and was washed with ether, then dehydrated with absolute alcohol, again digested with ether, and dried completely over sulphuric acid. Twenty and two-tenths grams of proteid were thus obtained equal to 4.04 per cent of the flour. We may therefore assume that this barley flour contained about four per cent. of the alcohol-soluble proteid, hordein.

#### PROTEID INSOLUBLE IN WATER, SALINE SOLUTIONS, AND ALCOHOL.

The proteids thus far described form only a part of the total proteids of the seed. One hundred grams of barley flour were extracted, first, with a large excess of five per cent. salt solution and then, repeatedly, with hot seventy-five per cent. alcohol. The residue, washed with absolute alcohol and thoroughly air-dried, weighed seventy-one grams and contained 1.07 per cent.



of nitrogen. The air-dry flour, before extraction, contained 1.83 per cent. of nitrogen. The 100 grams of flour therefore contained 1.83 grams of nitrogen and the residue, after extraction, contained 0.76 grams. The nitrogen removed by the solvents therefore amounted to 58.3 per cent. of the whole.

If we assume that the nitrogen all belonged to proteid-matter containing seventeen per cent. of nitrogen, the flour included 10.76 per cent of proteids, of which 58.3 per cent. was soluble in the reagents used in extracting the proteids already described. We have therefore  $10.76 - 6.28 = 4.48$  per cent. of proteid unextracted. It was only possible to obtain this proteid by treating the residue with potash water. All attempts, however, to thus prepare it in quantity sufficient to yield preparations of even approximate purity resulted in complete failure.

The previous extraction of the flour to remove the proteids already described seemed to render, to a great extent, the remaining proteid insoluble in potash water and only insignificant precipitates resulted on neutralizing the extracts. The barley flour also contained a large quantity of gum which rendered the filtration of the alkaline extract very difficult, as this gum dissolved freely in potash water. As the proteids prepared from the barley flour are all so similar to those obtained from wheat flour it is most probable that this seed also contains a considerable quantity of proteid soluble only in dilute alkaline solutions, but, as in the case of rye, the writer was unable to obtain results of any value whatever in regard to it.

#### CONCLUSION.

The barley kernel contains :

I. Leucosin coagulating at 52°, which is the same as the albumin found in the wheat and rye kernels. Its composition, as shown by the average of six analyses, is :

Carbon.....	52.81
Hydrogen.....	6.78
Nitrogen .....	16.62
Sulphur .....	1.47
Oxygen.....	22.32
	<hr/>
	100.00

This substance forms about three-tenths per cent. of the seed.

II. A small quantity of proteose, the reactions and composition of which could not be definitely ascertained.

III. Edestin, a globulin which is the same as that found in the wheat and rye kernels and in a large number of other seeds. Its composition is approximately shown by the figures given below. Owing to the small amount of this body and the difficulty in preparing it, no perfectly pure preparations were obtained.

Carbon .....	50.88
Hydrogen.....	6.65
Nitrogen .....	18.10
Sulphur }	24.37
Oxygen }	
	100.00

This is the proteid commonly known as vegetable vitellin. It is precipitated from saline solutions by dilution and by dialysis, is not coagulated by heating below 90°, and above that temperature only partially. It is not precipitated by saturating its solution with sodium chloride, but is thrown down from saline solutions by adding acid.

IV. Hordein, a proteid insoluble in saline solutions, very slightly soluble in pure water, and extremely soluble in alcohol of about seventy-five per cent. This is the barley proteid described by Ritthausen as mucedin. It has almost the same physical and chemical properties as gliadin obtained from wheat and rye kernels but a different composition.

Carbon .....	54.29
Hydrogen.....	6.80
Nitrogen .....	17.21
Sulphur.....	0.83
Oxygen.....	20.87
	100.00

About four per cent. of the seed consists of this substance.

V. After extracting the barley flour with salt solution and with alcohol the residue still contained forty-two per cent. of the total nitrogen, corresponding to proteid-matter equal to about four and five-tenths per cent. of the flour. It was not possible to extract more than a very small amount of this residual pro-

teid with dilute potash water, as the treatment for removal of the other proteids rendered it insoluble, if it were not so already.

VI. The barley flour contained 1.83 per cent. of nitrogen, and if it be assumed that this all belonged to proteid-matter with seventeen per cent. of nitrogen, the flour would contain 10.75 per cent. of proteids. The barley accordingly contained about four and a half per cent. of insoluble proteid, four per cent. of hordein soluble in dilute alcohol, three-tenths per cent. albumin, and 1.95 per cent. of globulin and proteose.

## THE DETERMINATION OF NITROGEN IN FERTILIZERS CONTAINING NITRATES.<sup>1</sup>

BY H. C. SHERMAN.

Received April 13, 1895.

AS soon as the accuracy of the Kjeldahl method for the determination of nitrogen was generally recognized, attention was turned toward the discovery of some simple modification by which it could be made applicable in the presence of nitrates.

Asboth (*Chem. Centrbl.*, 1886) recommended the simple addition of benzoic acid to the decomposing mixture. It was soon found that this method was not sufficient.

The following year, two methods were brought before the Association of Official Agricultural Chemists, one by Mr. Scovell, the other by Mr. Farrington. The principal difference consisted in the use of salicylic acid with the sulphuric acid to fix the nitrogen oxides by the former, while phenol was used for the same purpose by the latter. Both used zinc dust as the reducing agent. The Scovell method was adopted and remains practically unchanged.

In 1890, the Association sanctioned the use of zinc sulphide as a reducing agent. In case of its use the acid mixture was to contain one gram of salicylic acid instead of two. The use of zinc dust with two grams salicylic acid was retained.

In 1892, sodium thiosulphate, which had been used for reducing nitrates in the Ruffle method, was adopted as a third reducing agent, and it was directed that five grams of the crystallized salt should be added "direct."

<sup>1</sup> Read before the Washington Section.

In 1893, the use of zinc sulphide was dropped, (because this reagent was likely to contain nitrogen) and a modification of the Gunning method was adopted. In the latter, five grams of thio-sulphate and one gram of salicylic acid were used with the same amount of potassium sulphate as in the plain method (ten grams). It was claimed that that all the reagents could be added with the substance, but further trials disproved this, and in 1894 the requirement of first mixing the substance with the acid mixture was made practically the same as in the modified Kjeldahl.

It has been the experience of the writer, and the amount of work which has been done by the Association, indicates that it is the same with others, that the determination of nitrogen in fertilizers containing nitrates is attended with greater difficulty than in those free from nitrogen in this form. In the hope of discovering whether this is due to any considerable extent to the official methods, and, if so, the reasons therefor, the following experiments were undertaken.

A set of four samples was first prepared, composed of the following materials:

No. 1, sodium nitrate, ammonium sulphate, potassium chloride, acid phosphate.

No. 2, sodium nitrate, bone phosphate, dried blood, ammonite, marl filler.

No. 3, sodium nitrate, tobacco stems, cottonseed-meal, castor pomace.

No. 4, sodium nitrate, dried fish, natural guano.

In each case all the materials, except the nitrate, were first mixed, ground to pass through a five-tenths mm. sieve, and air-dried. Nos. 1, 2, and 3 were then mixed again, and the percentage of nitrogen carefully determined by both the Kjeldahl and Gunning methods. The guano used in preparing No. 4 contained a small amount of nitric nitrogen, and could not be determined in this manner.

An air-dried sample of sodium nitrate was then ground to pass through the same sieve, and its nitrogen content determined by the silica fusion method. This sample was then carefully mixed with those above described in such proportions as to give to each the desired percentage of nitrogen. Nos. 1, 2, and 3 were cal-

culated to contain ten per cent., eight and one-half per cent., and eight and one-half per cent. respectively. No. 4 was expected to show about eight per cent. These percentages are as high as are likely to be found in ordinary mixed fertilizers.

The materials employed represent all the general classes of ingredients commonly used in this section, and since no one of them composed less than fifteen per cent. of the mixture in which it occurred, any effect which it might tend to produce would be almost sure to be noticeable in the result.

The results on these mixtures by the official methods are given in Table I.

TABLE I. PER CENT NITROGEN FOUND IN KNOWN MIXTURES.

No.	Calculated.	Modified Kjeldahl Zinc dust.	Modified Gunning.
1.....	10.00	9.93	9.80
2....	8.50	8.51	8.50
3.....	8.50	8.48	8.50
4.....	...	8.12	8.08

Except in the case of No. 1, the figures given are the averages of two (and only two) determinations. The greatest difference between duplicates was 0.08 per cent.; the average difference 0.03 per cent.

Four determinations were made by each method on No. 1. These are given below.

The official methods as given on page 347 (Bul. 43, U. S. Dept. of Agr., Division of Chemistry) were followed closely with the following additional precautions.

1. In working the modified Kjeldahl method, the zinc dust was added through a funnel tube, very slowly, and with constant shaking. About two minutes is required to add the zinc dust in this way. After the first boiling, the flasks were allowed to cool somewhat before the mercuric oxide was added.

2. In the modified Gunning method, the boiling was continued about thirty minutes after the contents of the flask had become "nearly colorless."

To test these points determinations were made on Nos. 2, 3, and 4 without the precautions noted, but in every other way as above. The average results, together with those given above, are shown in Table II.

TABLE II. SHOWING EFFECT OF PRECAUTIONS NOTED ABOVE.

No.	Calculated.	Modified Kjeldahl:		Modified Gunning:	
		As above.	Zinc added in three to five portions and HgO at boiling heat.	As above.	Boiling stopped when nearly colorless.
2 .....	8.50	8.51	8.47	8.50	8.55
3 .....	8.50	8.48	8.46	8.50	8.36
4 .....	8.10 <sup>1</sup>	8.12	8.05	8.08	7.95
Av.	8.37	8.37	8.33	8.36	8.22

It is noticeable that the duplicates agreed about as closely as when the precautions were taken, but the results were in every case too low. The average discrepancy was, in the Kjeldahl, 0.04 per cent.; in the Gunning, 0.14 per cent. It would seem, therefore, that both of these precautions are advisable, and the second absolutely necessary, at least when working with high percentages.

Table III shows the results obtained on No. 1 by the modified Kjeldahl and Gunning methods, and by Winton's modification of the latter.

TABLE III. RESULTS ON SAMPLE NO. 1.

Calculated.	Modified Kjeldahl.	Modified Gunning.	Winton's Modification.
10.00	9.93	9.86	10.03
....	9.98	9.72	9.97
....	9.97	9.83	9.99
....	9.84	9.80	10.02
Average	9.93	9.80	10.00

The results by Winton's method are highly satisfactory; those by the Kjeldahl hardly so when compared with the other samples, while the Gunning gives results which are entirely too low to be called good.

Winton's modification of the Gunning-Kjeldahl method is essentially as follows: The substance is treated with the usual acid mixture and allowed to stand two hours, with frequent shaking. Two grams of zinc dust are then added and the first heating performed as in the Kjeldahl. Potassium sulphate is then added and the operation finished as in the Gunning method. It

<sup>1</sup> Average by both methods, see above.

is, therefore, a combination of the two with the improvement of the longer digestion in the acid mixture.

To return to the results on sample No. 1, since all the mixtures contain more or less phosphoric acid, the only substances peculiar to this sample are ammonium sulphate and potassium chloride. Since ammonium sulphate is formed in the process and is the final form of all nitrogen present, its presence in the sample could hardly account for the discrepancy, which, therefore, appears to be due to the chloride.

In looking over the record of the Association of Official Agricultural Chemists, we find that the modified Kjeldahl method has been tested by the Association in the year of its adoption and, with one exception, every year since on from one to five samples. Only four of these have contained chlorides, and only one in any considerable quantity. The modified Gunning has been tested by the Association on only one sample containing chlorides. These samples with the approximate percentages of chlorine, total nitrogen, and nitric nitrogen, and the variation in results reported, expressed in percentage of total nitrogen present, are shown in Table IV. All results which are so far from the average as to indicate accident are omitted, according to the custom followed by the reporters of the Association in averaging their results.

TABLE IV. ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.  
SAMPLES CONTAINING CHLORIDES.

Sample	Method	Chlorine, per cent.	Total Nitrogen, per cent.	Nitric Nitrogen, per cent.	Variation, per cent.
No. 4, 1888	Modified Kjeldahl	5	3.16	1.64	33.4
No. 1, 1889	" "	1.5	15.91	15.91	3.0
No. 3, 1889	" "	2.5	3.55	1.48	14.1
No. 2, 1893	" "	1.5	5.77	3.47	8.8
No. 2, 1893	Modified Gunning	1.5	5.77	3.47	7.5

To further test this question, determinations were made, in duplicate, on samples Nos. 2, 3, and 4, with one-half gram of potassium chloride added. Table V shows the average results with and without chlorides, the methods being carried out in exactly the same way as before.

TABLE V. PER CENT NITROGEN FOUND WITH AND WITHOUT CHLORIDES.

No.	Calculated.	Modified Kjeldahl.		Modified Gunning.	
		Without KCl.	With KCl.	Without KCl.	With KCl.
2 .....	8.50	8.51	8.37	8.50	8.35
3 .....	8.50	8.48	8.40	8.50	8.25
4 .....	8.10	8.12	8.04	8.08	7.92
Average	8.37	8.37	8.27	8.36	8.17

A portion of the sodium nitrate used in preparing these mixtures was now taken. It had shown by the silica fusion method 16.41 per cent. nitrogen. The modified Kjeldahl showed 16.39 per cent and 16.38 per cent.

Portions of one-half gram were taken for each determination, and mixed with the same amount of potassium chloride. The digestion was carried out in the usual way.

The results were :

Modified Kjeldahl.	Modified Gunning.
16.32	15.82
16.09	15.68
15.96	15.83
15.97	15.46
16.23	16.02 <sup>1</sup>
15.95	15.99 <sup>1</sup>
16.07	15.86 <sup>1</sup>
16.13	

The Winton modification was then tried and care taken to warm gently for some time after adding zinc dust before raising the heat, which was done gradually.

Results were :

16.27
16.30
16.30
16.34
Average 16.30

Indicating that the greatest care in the reduction process will not entirely prevent loss.

To ascertain more definitely at what stage in the operation the loss occurs, mixtures of one gram each sodium nitrate and potassium chloride were treated as in an analysis, and the gases escaping from the flask were made to pass through a bulb-tube

<sup>1</sup> Two grams salicylic acid used.



containing potassium hydroxide. The nitrates and nitrites thus recovered were converted into ammonia and estimated by means of Nessler's reagent, using for comparison a solution of ammonium chloride containing 0.0001 gram nitrogen in each cc. The operation was divided into four stages: (a) addition of sulphuric salicylic acid mixture; (b) addition of reducing agent; (c) gentle heating till frothing ceased; (d) brisk boiling for a few minutes. After evolution of gas had ceased in the first and second stages, and after removal of the flame in the fourth, a glass tube was inserted through the stopper reaching nearly to the surface of the liquid, the bulb-tube attached to an aspirator, and the gases contained in the flask thus drawn through the alkali. The following table (VI) shows the results obtained, expressed in terms of per cent. nitrogen on the basis of one gram substance:

TABLE VI  
Nitrogen Recovered.

Reducing Agent used.	Temper- ature.	a.	b.	c.	d.	Total.	b, c, and d.
Zinc dust .....	20°	0.023	0.006	0.026	0.008	0.063	0.040
" " .....	24°	0.027	0.005	0.034	0.013	0.079	0.052
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> in presence of K <sub>2</sub> SO <sub>4</sub> .....	22°	0.090	0.027	0.061	0.017	0.195	0.105
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> in absence of K <sub>2</sub> SO <sub>4</sub> .....	20°	0.090	0.027	0.035	0.013	0.165	0.075
Zinc dust <sup>1</sup> .....	27°	0.039	0.001	0.006	0.011	0.057	0.018

Where zinc dust was used the acid mixture contained two grams of salicylic acid; where thiosulphate was used, one.

The results indicate: 1. That the greatest losses occur on the addition of the acid mixture and on the first application of heat. The former is thought to be due to the liberation of hydrochloric acid in direct contact with the nitrate before the mass has become thoroughly wetted by the sulphuric salicylic acid mixture.

2. The total loss exclusive of the first stage is greater with thiosulphate than with zinc dust, and appears to be greater when potassium sulphate is added with the thiosulphate than when the latter is added alone. By exercising care in the addition of the reducing agent and the application of heat, the loss in the last three stages is reduced to a very small amount.

<sup>1</sup> Some precautions taken as in working Winton's modification on mixture of nitrate and chloride, see above.

3. At a given temperature, the loss on addition of acid is greater where the mixture containing less salicylic acid is used.

4. Using the same quantity of salicylic acid, the loss on addition of the acid mixture appears to increase with the temperature.

5. The total amount of nitrogen recovered being less than the average discrepancy showed by analysis under similar conditions, it appears probable that there may be some loss later on in the process.

These facts explain why the Kjeldahl gave better results on a mixture of nitrate and chloride than did the Gunning; while the Winton gave better than either.

In this connection the heat generated on the addition of the reducing agent is of interest. The average of seven determinations each on zinc dust and thiosulphate, both added in the usual way, showed, for the former, an increase of temperature of  $21^{\circ}$ ; for the latter, of  $40^{\circ}$ .

In the opinion of the writer, the prolonged digestion of the Winton method is useful, in the presence of chlorides, not only in securing complete solution of the nitrate, but also in allowing the contents of the flask to cool (for the heat generated by the action of the acid mixture on the chlorides is considerable) and to absorb a slight amount of moisture from the air, thus rendering the action less violent when zinc dust is added.

Mixtures of one-half gram each sodium nitrate and potassium chloride, treated with acid mixture cooled down to  $8^{\circ}$ , and digested as in the Winton method before addition of zinc dust, showed by the modified Kjeldahl method 16.34 per cent. and 16.32 per cent., or 99.6 per cent. of the amount found in the absence of chlorides.

Determinations by the modified Gunning on the same mixtures, in which the acid mixture was cooled to from  $8^{\circ}$  to  $12^{\circ}$ , the thiosulphate added slowly and with constant shaking and cooling of the flask, and the boiling continued some time after the liquid had become colorless, showed 16.02 per cent., 15.88 per cent., 16.16 per cent., and 15.99 per cent.; average, 16.01 per cent., or only 97.8 per cent. of the amount found when chlorides were not present.

Determinations on the same sample of pure nitrate alone by the modified Gunning method, carried out in slightly different ways, gave the following results :

As usually carried out with mixed fertilizers, 16.16 per cent. and 16.13 per cent.

Thiosulphate added first and heated before adding potassium sulphate, 16.16 per cent. and 16.24 per cent.

Thiosulphate added slowly with shaking and cooling, but digestion stopped as soon as liquid became colorless, 16.10 per cent.

Thiosulphate added as above, digestion continued one hour after colorless, 16.31 per cent. and 16.32 per cent.

As above, permanganate used, 16.37 per cent.

Modified Kjeldahl, using thiosulphate (five grams added direct), showed 16.37 per cent. and 16.36 per cent.

It may be well to state now that all the results given in this paper are corrected for reagents. At first a blank was run with every five determinations. After three or four such blanks had been made for each method and found to agree closely, their average was taken and applied to every result obtained by that method. Whenever it was necessary to change any of the reagents, another blank was run.

The results here given would *seem* to warrant the following conclusions.

1. For ordinary fertilizers containing little or no chlorides, the official methods are perfectly reliable if the directions are followed closely and the digestion in the modified Gunning is continued for at least a short time after the liquid has become practically colorless. The discrepancies which sometimes occur under these circumstances are believed to be due to faulty preparation of the sample.

2. In working with samples containing considerable amounts of chlorides, it is advisable to use the modified Kjeldahl (zinc dust) method and to cool the acid mixture before adding it to the substance. It appears advisable also to digest for some time at ordinary temperature before adding zinc dust. No way has been found by which equally accurate results can be obtained by the modified Gunning method in the presence of large amounts of chlorides, together with high percentages of nitric nitrogen.

3. When determining high percentages of nitric nitrogen by the modified Gunning method, it is necessary either to continue the boiling for some time after the contents of the flask have become colorless, or to use permanganate to complete the action.

MARYLAND AGRICULTURAL COLLEGE,  
COLLEGE PARK, MD.,  
February 20, 1895.

### ON CONDENSATION; AND ESPECIALLY ON THE CONDENSATION OF NITRIC ACID.<sup>1</sup>

BY EDWARD HART.

Received January 7, 1895.

THE ideal condenser, economically considered, is the one simplest in construction, most accessible for repairs or other purposes, and which, with a given efficiency, requires the least cooling liquid. The old-fashioned worm is certainly far removed from this ideal. The Liebig's condenser is a nearer approach. If the space between the inside and outside tube in Liebig's apparatus is made narrow enough it is possible to effect complete condensation in a relatively short tube, and to raise the cooling liquid to boiling temperature. At first sight it would seem that this gives a maximum efficiency; but it does not. If the water used as cooling liquid has, at the start, a temperature of  $0^{\circ}$ , and, as it issues from the condenser, a temperature of  $100^{\circ}$ , the heat absorbed by a given weight of water is approximately 100 units. If, however, the cooling liquid can also be made to evaporate, the heat absorbed is much larger in amount, and is equal to 100 units plus the amount required to evaporate it (526 units). This makes in all 626 units, or an efficiency six times as great. In the Liebig's condenser, also, the liquid condensed is cold or nearly so. In many cases this is not necessary and then an additional loss is sustained.

In the apparatus which I shall describe a very brief consideration will show that the maximum of efficiency may be attained. For, first, the cooling water is evaporated; second, the condensed liquid is boiling hot.

This condenser I have used in several modified forms adapted

<sup>1</sup> A paper with this title was read at the World's Congress of Chemists, Chicago, August 26, 1893. The present paper has been revised to accord with more recent experience and practice.

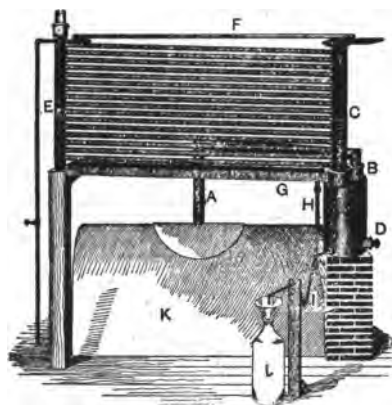
to various special purposes, among others, to the cooling of ammonia gas and the condensation of nitric acid.

In its simplest form, as used for preparing distilled water for example, the apparatus consists of a pipe with return bands placed one above the other, so that the vapor passes through the pipe in an upward direction, first right then left then right again, and so on, the bends rising one directly over another.<sup>1</sup> This pipe should be so large in diameter that the liquid may flow down in the lower part of the tube while the vapor is passing upward above it. For the same reason each bend of the pipe should have a slight rise so that the water may run down more rapidly. At the lower end the pipe should be enlarged and provided with an inverted siphon to act as a trap and carry off the condensed water. If, now, steam be passed up the pipe and water showered over the topmost bend, the water will, as it trickles down, become heated and evaporate. It is clear that by properly regulating the flow of steam and of water, we may secure complete condensation of the former and complete evaporation of the latter; at the same time the condensed water as it passes from the trap will have the boiling temperature. The cooling effect, if the apparatus is placed in the open air, is greater even than theory would predict for we have the additional cooling effect of the air. I have used this apparatus also for the separation of water vapor from ammonia gas, and for cooling the latter previous to condensing it. The conditions here are much the same as in the apparatus for distilled water. It is necessary to keep the condensed water at boiling heat to prevent reabsorption of ammonia, and in practice we find that very little ammonia is contained in this condensed water. The inclined tube acts besides as a very effective washer for the gas, completely removing any impurities mechanically carried over from the still. If it is desired to cool the condensed liquid, this is best done in a smaller apparatus of the same sort in which the current of liquid passes in an upward direction.

In the condensation of nitric acid the substances which can be used for the condenser are glass and stoneware, and it is therefore best to modify the apparatus somewhat, for the sake of sim-

<sup>1</sup> I have previously described a form of this apparatus which may be used for fractional distillation. See *Am. Chem. J.*, 6, 178.

plicity and for decreasing the pressure in the pipes, which causes loss and annoyance by leakage through joints, and pinholes in the stoneware. With this in view the stream of vapor has been subdivided by passing it through a number of glass tubes with slight fall sufficient to allow the condensed liquid to flow back into the receiver. In the apparatus shown in the figure, the



upright tubes at either side are made of stoneware, the connecting tubes are of thin glass. The pipe A, made of stoneware, carries the nitric acid vapors from the retort into the pot B provided with a stopper, D, which is taken out if frothing should occur and allows the froth to escape without danger of filling the condenser. The vapors pass up into C and are distributed

through the glass tubes luted into it. The condensed acid runs back and is discharged through the glass trap I into the container J.

The use of the glass tube is of great advantage since the color and amount of acid can be seen throughout the distillation and the firing regulated accordingly. From the pot the vapors ascend into the stoneware pipe and pass through the nearly horizontal glass pipes let into it into another similar stoneware tube on the left, from which the chlorine and lower oxides of nitrogen escape to the chimney or tower. These tubes are slightly inclined, and the acid condensing runs back into the pot. In running back it becomes very hot by contact with the vapors coming over and is deprived of the oxides of nitrogen. Condensation is effected by running water over the glass tubes from the perforated pipe above.

This apparatus is, to a certain degree, self-regulating. It never happens that the tubes condense the gas in equal amount. One of them is thinner or a little wider, and as condensation is more rapid the flow of gas into the tube is more rapid. But, in

any event, the pressure is equal in all the tubes, and only when the distillation is hurried too much will any uncondensed vapor pass through. There are fifteen tubes to each condenser about an inch in diameter and six feet long.

Two of these condensers have been in use for nearly two years at the works of Baker and Adamson, Easton, Pa., and the system has, therefore, had a thorough test. The retorts used here are cylindrical, as shown in the cut, and are made entirely of cast iron with iron heads. The niter-cake is drawn while fluid. These retorts each hold a charge of 1,000 pounds sodium nitrate. They are charged at 7 A. M. and the operation finished at 3. P. M., a *total of eight hours*. The best practice by the Griesheim system is, ordinarily, a charge of eight cwt. in twenty-four hours; under favorable conditions, and with a good fireman, sixteen hours are needed.

The floor-space required in this apparatus is reduced to a minimum. The condensers are, as shown in the cut, placed over and above one side of the brick arch which covers the cylindrical retort, so that absolutely no additional floor-space is required, all that is needed being sufficient room to pass conveniently between the retorts.

One man can run several retorts. All the assistance needed is that of a helper in discharging the retorts and in emptying the salt cake from the pans. These operations will require, perhaps, half an hour each.

In another place I have already (*J. Anal. Appl. Chem.*, 5, 382) pointed out the advantages of giving a cylindrical form to the retort, which requires less floor-space, less cost for masonry, and is less expensive in coal consumption. The form I have used is very much superior to, and quite different from, any of the patterns shown by Guttman (*J. Soc. Chem. Ind.*, 12, 203). In brief, this new form of condenser has the following good points:

1. It gives great efficiency with small first cost.
2. It requires but little water.
3. It requires but little floor-space.
4. It reduces the pressure and so reduces leakage.
5. It is easily and cheaply repaired.

## SOME POINTS IN THE DISTILLATION OF NITRIC ACID.<sup>1</sup>

BY EDWARD HART.

Received January 7, 1895.

IN a previous paper I described a tube condenser for use, among other things, in the condensation of nitric acid. Further experience with this condenser has enabled us to obtain still better results. We can now obtain a distillate very low in nitrogen peroxide. The specific gravities of the distillate are about as follows:

84 pounds.	1st distillate.....	Sp. gr., 1.527
83 "	2nd "	1.526
83 "	3rd "	1.523
82 "	4th "	1.512
77 "	5th "	1.504
77 "	6th "	1.493
74 "	7th "	1.487
74 "	8th "	1.485
47 "	9th "	1.474
47 "	10th "	1.448
57 "	11th "	1.300
785 "		

The amount of fuel necessary is surprisingly low if proper care is taken. For the distillation of 1,000 pounds nitrate, we use regularly but 150 pounds of pea anthracite coal, working day turn only; this is, no doubt, largely due to the short time within which the distillation has been brought by the use of this condenser, the distillation proper occupying but six hours, and the entire time, including charging and discharging, eight hours. During the night the retort and masonry, of course, cool off. I have no doubt that by running two shifts—day and night—the coal necessary could be brought within 125 pounds for the same weight of nitrate.

*Source of the Nitrogen Peroxide Produced.*—The contrast in color between nitric acid produced on the small scale in glass, and that made on the large scale in iron retorts, is very noticeable and I have been at some pains to look into the cause, since this formation often represents a dead loss to the manufacturer. I shall later on call attention to a period in the ordinary distillation during which, with no increase in the firing, the acid

<sup>1</sup> Read at the Boston Meeting, Dec. 27, 1894.

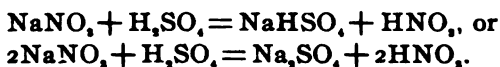


comes over very rapidly. It has often been noticed that during this stage, the acid is unusually white. I attribute this to the rapidity with which the gas passes from the retort, and consequent decrease in decomposition caused by the radiated heat. The same thing is noticed by distilling in glass. Certainly, therefore, part of the nitrogen peroxide is due to too long heating of the vapor, and the importance of an efficient condenser and a rapid distillation is evident.

The effect of concentration of the vitriol on the color is very evident. The ease with which concentrated nitric acid is decomposed is well-known and, as might be expected, the strong acid made from distilled vitriol and dry nitrate shows much stronger color than that made from the less concentrated materials. In glass, heating over a Bunsen, such acid may be obtained without difficulty of only a pale straw color, but in the ordinary iron retort the crude aqua fortis will frequently contain as much as three per cent. nitrogen peroxide.

It is the common opinion among acid makers that part of this color, perhaps a large part, is due to action of the acid on the iron. In most cases this is no doubt true, as the retort, as ordinarily set, is but imperfectly heated at the ends. In the retorts which I have been using, however, the retorts are *entirely* surrounded with the fire gases. It is quite possible, however, that even here the iron is notably attacked. Part of the color, no doubt, arises from impurity of the materials—chlorine, organic material, and iron in solution principally—but I suspect that this is responsible for only a part of the trouble. A gentleman who has for years carried on the distillation of nitric acid on the large scale, recently informed me that he had distilled fused nitrate and white vitriol in iron with no perceptible diminution of the color in the product.

As stated in the books, the only reactions occurring are



In practice only the first reaction is usually employed, especially where, as in acid for mixed acids, to be used for nitroglycerol, the product must be as concentrated as possible. In this

connection, however, one point I think should be noted that seems to have escaped attention, that is, that with weak vitriol the water is largely retained by the cake until the last stage of the operation, and greatly assists the decomposition giving a fair acid and a cake which is practically infusible. If, however, strong vitriol is used, the decomposition is incomplete and the acid exceedingly red.

*The Frothing.*—This matter of frothing is one that frequently gives great trouble to the nitric acid distiller, especially where weak acid and wet nitrate are used. The frothing begins in such cases after about seven-elevenths of the acid has distilled over.

This is easily demonstrated by conducting a distillation in glass with acid of 1.80 sp. gr., or less. The trouble becomes then plainly apparent, and is evidently due to the decomposition of the  $\text{NaHSO}_4$  at first produced into  $\text{Na}_2\text{S}_2\text{O}_3$  and water:  $2\text{NaHSO}_4 = \text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O}$ . That this is the reason may easily be demonstrated by heating in another similar retort a mixture of dry sodium sulphate and sulphuric acid. We then have  $\text{NaHSO}_4$  formed, and on continuing the heat the same frothing is noticed, although the distillate is, of course, entirely free from nitric acid. Frothing over is prevented by giving sufficient capacity to the retort, and by care and skill in firing. Neither alone is sufficient to prevent it.

*Rate of Distillation.*—One of the most remarkable things in the distillation, especially noticeable in glass and with pure dry materials, is the variation in the rate of distillation and the almost explosive evolution of acid, which takes place, for a short period, after about three-tenths of the acid has distilled over. For example: In distilling in glass 200 grams sodium nitrate and 235 grams distilled sulphuric acid, the proportions required by the equation  $\text{NaNO}_3 + \text{H}_2\text{SO}_4 = \text{NaHSO}_4 + \text{HNO}_3$ , the following results were obtained. It should be understood that the Bunsen, over which the operation was conducted, was allowed to remain untouched, except where noted, and that the apparatus was shielded from air currents. The thermometer bulb was shielded from radiation by placing it within a porcelain crucible in the retort.

Time.	Time interval.	Temperature.	Temperature interval.	Acid distilled.	Remarks.
1 : 46 : 40	.....	108°	...	..	Distillation begun.
2 : 48 : 23	1 : 43	110°	2°	5	
2 : 50 : 20	1 : 57	113°	3°	10	
2 : 52 : 30	2 : 10	117°	4°	15	
2 : 55 : 15	2 : 45	124°	7°	20	
2 : 59 : 00	3 : 50	128°	4°	25	
3 : 02 : 00	3 : 00	133°	5°	30	Froth rises.
3 : 02 : 55	0 : 55	125°	—8°	35	Froth very high.
3 : 03 : 30	0 : 35	125°	0°	40	Froth sinking.
3 : 04 : 00	0 : 30	125°	0°	45	No froth.
3 : 04 : 45	0 : 45	126°	1°	50	No froth.
3 : 17 : 40	12 : 55	135°	9°	55	{ Mushy mass fusing to clear liquid below.
3 : 23 : 30	5 : 40	148°	13°	60	Half fused.
3 : 38 : 30	.....	157°	9°	65	Three-fourths fused.
3 : 45 : 20	.....	152°	—5°	70	{ Piece of cake dropped into fused mass, lowering temperature.
3 : 52 : 00	.....	158°	{ Acid not running, clear fusion, lamp turned up.		
3 : 58 : 30	.....	170°	12°	75	No froth.
4 : 03 : 00	.....	178°	8°	80	No froth.
4 : 04 : 45	.....	180°	Lamp turned still higher.		
4 : 06 : 00	.....	194°	14°	85	Slight froth.
4 : 08 : 15	.....	200°	6°	90	Half-inch froth.
4 : 12 : 20	.....	220°	20°	20	{ Retort full of froth during this interval.
4 : 16 : 00	.....	246°	26	96	{ Froth gone, lamp turned out.

The drop of the temperature at 133° is, I think, unmistakable, and reminds one of the rise of temperature produced in the crystallization of a supersaturated solution. There we have the change from the fluid to the solid condition—here from the solid to the fluid. This explosive evolution is noticeable also in distilling in iron on the large scale and, perhaps, explains in part the difficulty nitric acid makers have hitherto had in properly condensing their product. By proper firing, and with a properly set retort, this difficulty is lessened.

To decompose strong nitric acid by heat or by its action on iron, and then to drive off the nitrogen peroxide with great pains and loss, is evidently a clumsy and probably unnecessary operation. I shall, therefore, make a determined effort to so arrange the retort that this will be in future unnecessary. There would seem to be no insuperable obstacle in the way of so conducting the distillation that even the first distillate would be of a pale straw color, like that made in glass, and quite fit for the manufacture of dynamite and other nitro compounds with no purification whatever.

The use of nitro compounds has, of late years, become so large that a rational method of conducting the process of nitric acid distillation is imperatively called for.

Berthelot has shown that strong nitric acid is completely decomposed at about  $360^{\circ}$  into nitrogen peroxide, oxygen, and water. It is certain that with the retorts entirely surrounded by fire gases the temperature of the upper part of the retort exceeds  $100^{\circ}$ . It is not surprising, therefore, that the first distillate should show a dark red color. A recent distillation in glass, with pieces of cast iron immersed in the mixture of acid and nitrate, gave no additional color to the first distillate.

---

### NEW BOOKS.

COD-LIVER OIL AND CHEMISTRY. BY F. PECKEL MÖLLER, PH.D. London: Peter Möller. New York: Wm. H. Schieffelin & Co. Printed for private distribution.

This book is really two books in one. The first part treats of cod-liver oil, the methods of catching the fish, the preparation of the oil, and an account of its constituents. We learn that cod-liver oil was originally made from fresh cod-livers by the steam process, by Peter Möller, in 1853. The oil so prepared was a great improvement over the older product prepared by the putrefaction of the livers. It still, however, caused disagreeable after-effects when exhibited, and to remedy this an investigation was undertaken by P. M. Hyerdahl, presumably in the employ of Peter Möller. Mr. Hyerdahl finds that the disagreeable after-effects are caused by the presence of hydroxy acids in the oil, and that these may be excluded by rendering the livers in an atmosphere of carbon dioxide. This process is now carried out by Peter Möller, therefore buy your cod-liver oil of this firm. The deduction is not so stated in the book, which is well written and gives a very readable account of the subject, but the advertising purpose is obvious.

It is a pity that Mr. Hyerdahl's work was not made known through the regular channels—the *Berichte* for example. Chemists will be apt to look with suspicion upon statements so obviously interested.

The second part of the book is a treatise on organic chemistry of an original sort. The author has used the Daltonian symbols in modified form, and the result is, as might have been expected, that the poor devil of a printer has had a hard time of it. So long as printing is done as at present, authors should beware of using new characters; by so doing they not only increase the already difficult task of the printer but really put themselves at his mercy. If only one printer have the character he must be allowed to do the printing of course. While such symbols have certain advantages, their disadvantages seem greater. Only a few people seem to be able to remember that, after all, our symbols represent only very imperfect knowledge, and that they are only tentative. A chemist can, therefore, read this treatise with interest and profit; it can scarcely be considered a good book for beginners, but it was probably not intended for beginners.

EDWARD HART.

THE INCREASE IN WEIGHT OF TIN AND LEAD ON CALCINATION. BY JEAN REY, 1630. Alembic Club Reprints, No. II. 54 pp. Edinburgh: William F. Clay, 1894.

Rey is one of the less well-known investigators of the seventeenth century. He is properly to be classed with Hooke, Mayow, and Boyle, or the Oxford School of Chemists, as Thorpe has fitly called them, in their work upon the increase of weight of the metals when calcined, and the part played by the air in these processes. That which Thorpe has so well done for the others is now done for Rey in this little book. The quaintness of the original is well preserved in the translation, and the book is very valuable as giving an insight into the wisdom and the childishness of the times. His self-applause in the triumphant summing up of the evidence in support of his theory, that the air played an important part in the phenomena observed, is delicious.

The Alembic Club is doing a most valuable work for the science in the republication of these early essays. They are interesting and helpful to the earnest student and should have a wide circulation.

F. P. VENABLE.



# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

---

### THE CHEMICAL NATURE OF DIASTASE.<sup>1</sup>

BY THOMAS B. OSBORNE.

Received April 2, 1895.

FEW substances are of more importance or of more interest than the enzymes or unorganized ferments, yet our knowledge relating to these bodies is almost wholly confined to the products of their activity and the conditions under which this is manifested. Although the existence of these ferments was recognized early in the present century, our information in respect to their true nature is exceedingly limited and unsatisfactory. It was for a long time supposed that the active substance causing a fermentative change is a soluble proteid, and the power of inducing such change seems by many to have been ascribed to soluble proteid matter in general. Later, this power was thought to be restricted to special forms of proteid, but no sufficient evidence was brought forward. Of late years investigators have undertaken to isolate ferments and prepare them in a state of purity. The results of these attempts have led to very conflicting conclusions respecting the character of these bodies. Some of the so-called pure preparations of ferments have had the properties of the proteids, and have more or less agreed with them in composition, while others have differed widely from the proteids in both respects.

It still seems to be the opinion of many that the enzymes are

<sup>1</sup> Read before the New York Section, December, 1894. Reprinted from the Report of the Connecticut Agricultural Experiment Station, 1894.

in fact true proteids and that the ferments thus far supposed to be obtained in a state of purity were simply somewhat contaminated with other substances. This opinion is based on the fact that all those changes which are ascribed to the action of enzymes occur only in solutions which contain proteid matter, and that the activity of the ferment is greatly influenced by conditions known to have a pronounced action on proteids, such as heat, the presence of acids and alkalies, salts of the heavy metals, etc.

The first discovered and one of the most carefully studied of these ferments is diastase. The practical application of the action of diastase in the manufacture of alcohol and of malt liquors has given rise to careful and extended studies of the conditions affecting the activity of this ferment, and the result of these studies has led some to the opinion that the active substance is the albumin present in the malt extracts. The conversion of starch into maltose and dextrin by diastase increases in rate and extent as the temperature of the solution is raised, until the heat reaches the point at which the albumin begins to coagulate. The ferment then begins to lose power, and, when the heat is sufficient to completely coagulate the albumin, its amylolytic action ceases entirely. In 1883, C. Lintner, Jr., showed that the diastatic power of fifteen different samples of malt was very nearly proportional to the amount of coagulable albumin which they contained. In 1886, however, C. J. Lintner prepared diastase in, as he supposed, a state of purity, and came to the conclusion that the results of his analysis of diastase indicate that, in the ferments, we have a special class of proteid substances. The composition of Lintner's purest diastase differed much from that of the proteids, since it contained only two-thirds as much nitrogen and also less carbon. His diastase furthermore, failed to give the reaction with cupric sulphate and potassium hydroxide which is characteristic of proteid matter. These results of Lintner's threw much doubt on the hypothesis that the vegetable albumin is identical with diastase.

In my investigations of the proteids of wheat, rye, and barley, I found in all these grains the same albumin and was impressed with the close relation between the temperature at which this albumin coagulates and the temperature at which diastase begins



to lose its activity. The aqueous extracts of these seeds, as is well known, possess considerable diastatic power, and it seemed to be more than probable that this was due to the albumin. I accordingly undertook an investigation of this subject, and I now offer the results thus far obtained, which are preliminary to a more extended study.

The usual method of preparing vegetable enzymes is to treat the aqueous or glycerol extract containing them with alcohol as long as a precipitate, having fermentative power appears, to purify this by repeated precipitation from its solution in water, by means of alcohol, and finally to subject the aqueous solution to dialysis to remove salts. This method is wholly unsuited to yield pure preparations, because the precipitate produced by alcohol contains not only a large amount of carbohydrates and salts, but also nearly all of the various forms of proteid matter present in the extract. Lintner employed this method, and there can be no doubt that he obtained a mixture of proteids with other substances which defied all attempts at further separation.

The most rational method (hitherto very little used) is first to separate the proteids from the carbohydrates and other soluble substances by saturating the extract with ammonium sulphate, thereby precipitating the ferment and proteids together, next to remove the proteid existing as globulin, by dialysis, and then, if possible, to separate the albumin and proteoses by fractional precipitation with alcohol. In following this method, a measured quantity of malt extract was saturated with ammonium sulphate, the precipitated proteid matter was filtered out, dissolved in water, and the clear filtered solution made up to the volume of the original extract. This solution was found to have the same diastatic power as before precipitation, thus showing that ammonium sulphate had not injured the diastase. Throughout my work diastatic power has been measured by Lintner's method, which gives a very ready means of accurately comparing different preparations. This method consists in adding to each of a series of carefully measured volumes of the solution containing definite amounts of the diastatic preparation, ten cc. of a two per cent, solution of soluble potato starch, and allowing the ferment

to act upon the starch for one hour at the ordinary temperature of the room. At the end of this time five cc. of Fehling's solution are added to each portion and the mixtures are heated for ten minutes in a boiling water-bath. After the precipitated cuprous oxide has settled, where too little sugar has been formed to precipitate all the copper, the liquids will be blue; if sugar is in excess they will be yellow. The one colorless liquid that should result gives the measure of diastatic power. Lintner represented the value of his most active preparation by 100, and that of the other preparations by figures stating the amount of each necessary to give a complete reaction with Fehling's solution under the above conditions, in comparison with his most active preparation, of which, under the conditions of the test just described, twelve one-hundredths of a milligram completely reduced the five cc. of Fehling's solution.

For the sake of comparison I have measured the activity of my preparations by the same standard, so that a preparation whose activity is given as 200 means that six one-hundredths of a milligram sufficed to give a complete reduction.

As Lintner recommended extracting the malt with water containing twenty per cent. of alcohol instead of pure water, since thereby less foreign matter was removed with the proteid, this procedure was first tried. Fifteen hundred grams of ground air-dried malt, prepared in the laboratory, were treated with three liters of twenty per cent. alcohol, the extract squeezed out in a press, and the residue again treated with another liter of the same dilute alcohol. Three liters of extract were obtained which, after being filtered clear, were saturated with ammonium sulphate. Owing to the presence of the alcohol much less ammonium sulphate was dissolved than by a water extract, and the proteids were consequently incompletely precipitated. The precipitate obtained was treated with water and a considerable quantity of insoluble matter, consisting mostly of globulin, rendered insoluble by contact with the reagents, was filtered out. The solution was saturated with ammonium sulphate, and the precipitate dissolved in water. This clear solution was then dialyzed in water for some days, and after filtering from a slight deposit was dialyzed in alcohol of 0.845 sp. gr. for forty-eight hours. •

As the water passed out of the dialyzer faster than the alcohol entered, the solution became concentrated and a considerable precipitate formed. This was filtered out and washed, first with dilute alcohol and afterwards with absolute alcohol, and dried over sulphuric acid. This preparation, 1, when thus dried, dissolved in water with the exception of a not inconsiderable residue. When filtered clear, the solution, on heating, gave an abundant coagulum, and after boiling and filtering out the coagulum, the filtrate gave a strong pink color with cupric sulphate and potassium hydroxide, showing the presence of proteose. The diastatic power of this preparation, in comparison with Lintner's best was eighty-six, but, as it was afterward found to contain a comparatively small amount of ash, the test was repeated with the addition of a few milligrams of sodium chloride and then found to equal 150.

The composition of preparation 1 was as follows:

PREPARATION 1.		Ash-free.
Carbon .....	52.55	
Hydrogen .....	6.48	
Nitrogen .....	16.41	
Sulphur } .....	24.56	
Oxygen }		
		100.00
Ash.....	2.29	

These figures indicate that this preparation consisted almost wholly of proteid matter, and the reactions proved the presence of at least three forms; namely, coagulated proteid, albumin, and proteose. This mixture was one and a half times more active than Lintner's most energetic preparation, and contained about six per cent. more nitrogen and one-half as much ash. The composition of the preparation is very similar to that of the coagulated albumin-like body obtained from wheat, rye, and barley, and for which I have adopted the name leucosin. As this albumin has been found to have the same composition, whether coagulated by heat or by alcohol, and as most, if not all of the proteids have identical composition (so far as analysis can show), in the soluble and the coagulated states, it seems probable that

preparation 1 consisted mostly of coagulated and soluble leucosin together with a little proteose.

The filtrate from this preparation on addition of absolute alcohol, yielded a small precipitate, 2, which dissolved wholly in water and gave only a very slight coagulum on heating, but a strong pink biuret reaction, showing it to be mostly proteose. Its diastatic power was only nineteen.

As above stated, owing to the presence of alcohol, saturation of the original extract of malt with ammonium sulphate, precipitated only a part of the proteids. Accordingly the filtrate from this first precipitation was dialyzed for twenty-four hours, so as to remove most of the alcohol, and was again saturated with ammonium sulphate. The resulting precipitate was dissolved in water, filtered from a slight residue, and the clear solution dialyzed until nearly all the ammonium sulphate was removed. The dialyzer was then transferred to alcohol and left for forty-eight hours. The resulting precipitate was then filtered out and treated in the manner before described. After drying, this substance, preparation 3, like preparation 1, consisted of insoluble proteid, soluble leucosin, and proteose. Its diastatic power was 133, and it had the following composition:

PREPARATION 3.

	Ash-free.		Average.
	I.	II.	
Carbon.....	52.34	....	52.34
Hydrogen.....	6.73	....	6.73
Nitrogen.....	15.90	15.92	15.91
Sulphur } .....	....	....	25.02
Oxygen }			
			100.00
Ash .....			0.82

The filtrate from this preparation was next treated with a large quantity of absolute alcohol, and the contained proteid completely thrown down. This substance, preparation 4, dissolved entirely in water; its solution yielded but a trace of coagulum on heating, and when boiled and filtered gave a strong proteose reaction. It contained, ash-free, only 12.02 per cent. of nitrogen, and had a diastatic activity of 11.

These results prove that extraction of the malt with twenty per cent. alcohol is not suited for a subsequent precipitation of the proteids with ammonium sulphate; that otherwise the method is capable of yielding preparations of diastase of high fermentative power, which to a certain extent can be separated into fractions containing the different forms of proteid matter; that the fractions including the greatest amount of soluble albumin have the greatest diastatic power; and that a part at least of the proteose is almost, if not entirely, free from this power.

Another extraction was made on a much larger scale, so that the fractional precipitations might be more numerous, and the fractions examined more closely.

Ten kgms. of malt were exhausted with water and the extract was saturated with pure and neutral ammonium sulphate. The very bulky precipitate was suspended in four liters of water and dialyzed until much of the sulphate had been removed and the precipitated proteid largely dissolved. The solution was then filtered from an insoluble residue consisting mostly of globulin, and the clear filtrate was saturated with ammonium sulphate. The precipitate thus obtained was suspended in 1500 cc. of water and was dialyzed until nearly all the sulphate had been removed and the precipitate mostly dissolved. The globulin contained in the extract was thus largely separated and, after it had been filtered out, the clear solution was dialyzed into an equal volume of alcohol of 0.84 sp. gr. After forty-eight hours the precipitate, number I, which had separated, was filtered out and set aside for further examination. The filtrate was again dialyzed into an equal volume of alcohol of 0.84 sp. gr., and after forty-eight hours another precipitate, II, obtained. The filtrate was further dialyzed into a rather large quantity of somewhat stronger alcohol, and precipitate III separated, and by similarly treating the filtrate from this, precipitate IV was obtained, the filtrate from which, on adding a large quantity of absolute alcohol, yielded precipitate V. All the proteid in the extract was thus separated. Precipitate I was much contaminated with coloring-matter, II less so, and III was nearly colorless, as were also IV and V.

The approximate weights of each of these precipitates was as

follows: I, thirteen grams; II, eight; III, six; IV, five; and V, three, a total of thirty-five grams.

Precipitate I was treated with water and found to be very largely insoluble. The insoluble matter was filtered out and washed with water, and the clear solution was dialyzed for several days to remove all the salts. No proteid was thus precipitated, and the dialysis was continued in strong alcohol, thereby throwing down all but a trace of proteid. The precipitate, preparation 5, weighed 2.11 grams. After drying, it dissolved in water with the exception of a small residue, and its solution when slowly heated became turbid at 65° and deposited flocks at 70°. After boiling and filtering out the slight coagulum, the solution gave a strong pink reaction with the biuret test. These tests show the preparation to consist largely of proteose. Its composition was as follows:

PREPARATION 5.		Ash-free.
Carbon .....	53.16	
Hydrogen .....	7.03	
Nitrogen .....	16.50	
Sulphur .....	1.50	
Oxygen .....	21.81	
		100.00
Ash .....	0.49	

With Lintner's test this preparation showed a diastatic power of thirty.

The insoluble residue, remaining after treating precipitate I with water, was thoroughly extracted with ten per cent. sodium chloride solution; what remained insoluble in this menstruum was filtered out and the clear solution dialyzed until free from chlorides. The precipitate thus formed, preparation 6, weighed one and two-tenths grams, and after drying was not soluble in water, but dissolved readily and nearly completely in salt solution, having, as was to be expected, the properties of a globulin. This substance had a very slight diastatic power, and its sodium chloride solution when heated slowly became turbid at 60°, a few flocks appearing at 65°, due to a trace of albumin. Its composition was as follows:

## PREPARATION 6.

	Ash-free.
Carbon .....	53.11
Hydrogen .....	6.45
Nitrogen .....	15.78
Sulphur } .....	24.66
Oxygen } .....	
	<hr/>
	100.00
Ash .....	0.75

The filtrate from preparation 6 still contained proteid matter which was separated by dialysis in alcohol. Preparation 7 was so obtained, weighing 1.54 grams, having the same properties as 6, and the following similar composition :

## PREPARATION 7.

	Ash-free.
Carbon .....	53.58
Hydrogen .....	6.70
Nitrogen .....	15.87
Sulphur } .....	23.85
Oxygen } .....	
	<hr/>
	100.00
Ash .....	1.43

After extracting precipitate I with water and salt solution a very considerable part still remained undissolved. This was treated with water to remove all the salt, and then with alcohol, and was dried over sulphuric acid. This preparation, 8, weighed eight grams and was quite dark in color. It had the properties of an insoluble form of globulin, being dissolved in one-half per cent. sodium carbonate solution and precipitated therefrom by neutralization. Its composition was nearly the same as that of the two last globulin-like preparations and is probably a so-called "albuminate" derived from that substance. The composition of preparation 8 was :

## PREPARATION 8.

	Ash-free.
Carbon .....	53.55
Hydrogen .....	7.01
Nitrogen .....	15.72
Sulphur .....	1.23
Oxygen .....	22.49
	<hr/>
	100.00
Ash .....	1.09

Precipitate II was treated with water and the solution thus

formed was dialyzed in water for several days and then in alcohol for twenty-four hours. A quantity of absolute alcohol was finally added to the contents of the dialyzer, thus completely precipitating the proteid. This preparation, after drying, was almost wholly soluble in water, and when heated slowly its solution became turbid at 60° and deposited flocks at 66°. The amount of proteid thus coagulated was somewhat greater than was given by preparation 5, and its diastatic power was likewise greater, being seventy-five. Analysis showed its composition to be as follows :

## PREPARATION 9.

	Ash-free.
Carbon.....	53.19
Hydrogen.....	6.71
Nitrogen.....	16.74
Sulphur.....	1.38
Oxygen.....	21.98
	<hr/>
	100.00
Ash.....	0.78

This preparation contained a slight amount of insoluble matter, some albumin and much proteose.

The residue of precipitate II, which was not dissolved by water, was treated with sodium chloride solution and the clear extract dialyzed till free from chlorides, but as no precipitate was produced, the dialyzer was transferred to alcohol when preparation 10 separated, weighing 0.49 gram, and containing, ash-free, 15.18 per cent. of nitrogen. It is probable that this is the same globulin obtained in larger quantity from precipitate I, but less pure. That part of precipitate II which remained undissolved after extracting with water and salt solution, was then washed thoroughly with water and with alcohol, yielding preparation 11, which weighed 5 grams and had the following composition :

## PREPARATION 11.

	Ash-free
Carbon.....	53.51
Hydrogen.....	6.75
Nitrogen.....	15.76
Sulphur.....	1.12
Oxygen.....	22.86
	<hr/>
	100.00
Ash.....	0.66



These figures show that precipitate II contained less globulin and proportionately more leucosin and proteose than precipitate I and it was accordingly found to be more powerfully diastatic.

Precipitate III was in turn treated with water, the resulting extract filtered clear, dialyzed for several days in water, and then in alcohol, absolute alcohol being finally added in quantity to the contents of the dialyzer. The resulting precipitate, preparation 12, weighed three grams. It was almost completely soluble in water, and its solution when slowly heated became turbid at 55° and flocculent at 60°. The amount of this coagulum was much greater than that yielded by preparation 9. The filtrate from the coagulum gave a strong proteose reaction. The diastatic power was 222, indicating the presence of much more diastase than any of the preceding preparations. Its composition was as follows :

## PREPARATION 12.

	Ash-free.
Carbon .....	52.80
Hydrogen .....	6.96
Nitrogen .....	16.09
Sulphur .....	1.45
Oxygen .....	22.70
	<hr/>
	100.00
Ash .....	0.59

The residue of precipitate III was digested with salt solution, the filtered extract was dialyzed in water till free from chlorides, and then, as no proteids separated, the dialysis was continued in alcohol. Only 0.28 gram of proteid resulted, which, without correction for ash, contained 12.53 per cent. of nitrogen. This was marked preparation 13, and considered to be impure globulin.

The part of precipitate III still undissolved was washed with water and with alcohol, yielding preparation 14, which weighed 2.87 grams. This had the following composition :

## PREPARATION 14.

	Ash-free.
Carbon .....	53.25
Hydrogen .....	7.65
Nitrogen .....	16.12
Sulphur .....	1.38
Oxygen .....	21.60
	<hr/>
	100.00
Ash .....	0.55

This preparation has a somewhat higher nitrogen and lower carbon content than preparations 8 and 11, which is probably due to its being a mixture of the insoluble form of the globulin with some insoluble albumin coagulated by the long contact with alcohol to which it had been subjected. This is to be expected, as precipitate III contained relatively more albumin than precipitates I and II.

Precipitate IV was next treated with water, the solution filtered clear, dialyzed for some days in water, and afterwards transferred to alcohol, and the dialysis continued. Absolute alcohol was then added to the contents of the dialyzer, giving preparation 15, weighing four grams. This substance dissolved in water to a nearly clear solution, which, when filtered perfectly clear and heated carefully, became turbid at 50° and gave a large coagulum at 56°. After heating the solution and filtering off the coagulum, a good reaction for proteose was obtained with the biuret test. This preparation had a diastatic power of 600. As this was a much more powerful ferment than any yet produced, its properties were carefully studied and will be described at length later. When analyzed this substance was found to have the following composition :

PREPARATION 15.		Ash-free.
Carbon .....	52.50	
Hydrogen .....	6.72	
Nitrogen .....	16.10	
Sulphur .....	1.90	
Oxygen .....	22.78	
		100.00
Ash .....	0.66	

It will be noticed that the sulphur in this preparation is a little higher than in the preceding preparations, which is probably due to its containing some sulphate.

The part of precipitate IV which did not dissolve in water was treated with salt solution, but no globulin was extracted. The residue was then washed with water, giving preparation 16, which weighed 0.9 gram and had the following composition :

## PREPARATION 16.

	Ash-free.
Carbon .....	53.42
Hydrogen .....	7.15
Nitrogen .....	16.65
Sulphur } .....	22.78
Oxygen } .....	
	100.00
Ash .....	0.24

The composition of this insoluble product shows it to be probably coagulated leucosin.

A portion of precipitate V, when treated with water, was found to dissolve completely. It was therefore washed with absolute alcohol, yielding preparation 27, which weighed 2.87 grams. The clear solution of this substance when heated became turbid at 50°, and yielded a small coagulum at 58°. Boiled and filtered, a strong pink coloration was given with the biuret test, thus showing it to consist mostly of proteose. The diastatic power of this substance was 60, only one-tenth that of preparation 15. Its composition was :

## PREPARATION 17.

	Ash-free.
Carbon .....	51.21
Hydrogen .....	6.52
Nitrogen .....	15.40
Sulphur } .....	26.87
Oxygen } .....	
	100.00
Ash .....	2.37

The lower nitrogen content of this preparation indicates that the strong alcohol had thrown down, together with the proteids, some non-nitrogenous substances.

Much is to be learned by studying these results which will be of service in future attempts to isolate pure diastase.

In the first place, it is plain that we have in our malt extract a globulin, an albumin, and at least one, more probably two, forms of proteose. I believe the substance soluble in salt solution to be a true globulin, since it so readily assumes an insoluble form, and also because a much larger quantity of the same

body was obtained by extracting with ten per cent. salt solution, the malt residue remaining after the extraction with water. I also think that at least two forms of proteose are present, for the water-soluble portion of precipitate I consisted chiefly of proteose, as did also precipitate V. The amount of proteose diminished from precipitate I to precipitate IV, which contained the least, while precipitate V, which, it will be remembered, was thrown down by adding to the solution a very large amount of absolute alcohol was mainly proteose. A part of the proteose was precipitated by alcohol more readily than the albumin, while another part was less readily precipitated. Beside the albumin, globulin, and proteose, we have also to take account of the "albuminate" or insoluble forms of the albumin and globulin. The results of this extraction show that the globulin is rendered insoluble more rapidly than the albumin, so that precipitation with alcohol and solution in water, repeated a few times, may be depended upon to remove the former. Whether repeated fractional precipitation can be employed to completely separate the albumin from the proteoses is not so certain. The albumin is thrown down from the malt extract by saturation with magnesium sulphate, and it is not unlikely that a complete separation can be accomplished by this reagent. It is, however, not to be forgotten that the diastase may be a substance which, when heated to from  $50^{\circ}$ – $60^{\circ}$ , splits apart into an albumin and a proteose, and that the proteose found in the solutions which have been heated is a decomposition product of the diastase. Kühne's attempts to produce pure trypsin led him to suspect that this ferment is a body which, when heated, yields a coagulable fraction and a proteose-like substance. Hammarsten's more recent work on a neucleoproteid obtained from the pancreas also points strongly in this direction.

Now that we have some precise knowledge of the associated substances, it seems probable that we may succeed in obtaining diastase nearly, if not quite, pure, and arrive at a clearer and more positive knowledge of this ferment, and also have a guide in further study of other enzymes, which will lead to a more satisfactory understanding of this whole subject. It is probable that the ferments contained in seeds are much easier to prepare than

those of animal origin, since the substances with which they are associated are largely non-proteid and comparatively easy to separate. It is also certain that the amylolytic ferments present an easier problem than the proteolytic, for the products of the activity of the latter are so similar, in their nature, to that which the ferment is supposed to possess, as to make it always a matter of great uncertainty whether the separated enzyme is free from those bodies or not.

As already stated, preparation 15 was a very energetic ferment, and on this account its properties were more fully studied, with the following results:

Dissolved in water this substance gave all the usual proteid reactions, and when heated slowly became turbid at  $50^{\circ}$  and gave a flocculent coagulum at  $56^{\circ}$ . This is exactly the temperature of coagulation of the albuminum (leucosin) which I have prepared from wheat, rye, barley, and malt, with identical composition and properties. The aqueous extracts of these grains have, moreover, a strong diastatic action on starch. The amount of coagulable albumin in preparation 15 was determined and found to be 53.2 per cent. of the dry substance.

These facts point strongly to the albumin as being the diastatic substance, yet there are several facts hard to explain, if this be true, which cannot be overlooked. Although in general the diastatic power of my preparations was greater the larger the amount of coagulable albumin they contained, I have never yet been able to establish any numerical relations between the two. In no case have I found any diastatic action with solutions free from albumin. Furthermore, the activity of my preparation 15 is such as to require a much greater diastatic power for malt than this shows if its coagulable albumin is the enzyme.

A malt extract corresponding to a solution of the diastase in five milligrams of malt had the same diastatic power as 0.02 milligram of preparation 15. As the preparation contained but a little over fifty per cent. of coagulable albumin, this would correspond to only 0.01 milligram of albumin in the five milligrams of malt, or two-tenths per cent. The amount of albumin in malt is much greater than this, as it is also in wheat, rye, and barley, whose diastatic power is greatly inferior to that of malt. It is

not probable that the *separated* diastase is more active than that *in the seed*, especially in view of the experiments which follow, comparing the action of malt extract and preparation 15. The only explanation of this that occurs to me, is that the active diastase is a combination of albumin with some other body, presumably the proteose, which breaks up on heating, yielding coagulated albumin, and that, besides this combined albumin, free albumin is also present, which has no diastatic power, but which is coagulated at the same time. There is no direct evidence, however, that this hypothesis is correct.

Compared with other so-called pure ferments, preparation 15 is very active. At 20° it was in a condition to produce, from soluble starch, over 2000 times its weight of maltose and a further undetermined quantity of dextrin, within one hour. After having been dried over sulphuric acid and kept for six months, its activity was reduced to one-half, but in this condition it produced in seventeen hours, at 20°, 10,000 times its weight of maltose besides an unknown quantity of dextrin. At 45° the same quantity of maltose was produced in one hour as at 20°. At 50° much less and at 55° very little maltose was formed. These tests were made by using an amount of diastase solution just sufficient to produce enough maltose at 20° to exactly reduce five cc. of Fehling's solution.

Compared with malt extract of the same diastatic strength, as measured by the amount of maltose produced in one hour at 20°, the distilled water solutions of preparation 15 have a less powerful action in liquefying starch paste. Five cc. of malt extract added to ten cc. of a starch paste containing two per cent. of starch, dissolved the starch completely in eight minutes, while the solution of preparation 15 required thirty-seven minutes.

The malt extract is also more energetic in converting starch completely into bodies giving no color with iodine. Five cc. of the same malt extract added to ten cc. of soluble starch solution caused the blue reaction with iodine to disappear in thirteen minutes, while it required thirty-eight minutes to reach the same result with the solution of the separated diastase. When, however, the diastase was dissolved in malt extract, whose enzymes

had been previously killed by heating, the difference between the separated diastase and that in the malt extract nearly disappeared.

Two test-tubes were each charged with ten cc. of starch paste. To one tube were added five cc. of fresh malt extract, and to the other the same amount of boiled and cooled malt extract in which had been dissolved a quantity of preparation 15, sufficient to make a solution of the same sugar-producing power as the fresh malt extract itself.

The fresh malt extract liquefied the starch in seven minutes, the mixture of preparation 15 and boiled malt-extract in fourteen minutes, while thirty-seven minutes were required to produce the same result with a distilled water solution of preparation 15. In completely converting starch into bodies giving no color with iodine, the solution of preparation 15 in boiled malt extract gave exactly the same result as the fresh malt extract, showing that the difference first noticed was due to the conditions and not to the ferment.

In view of these results, it seems highly probable that diastase is a true proteid, for if we consider the extremely minute quantity of preparation 15 required to produce large amounts of maltose, it is hard to believe that this action is due to some substance adhering to the proteid to the extent of only three or four per cent. at the most. If such were the case it is also remarkable that the enzyme should adhere in so much greater quantity to the particular precipitate represented by preparation 15 than to any of the other numerous fractions. If diastase, then, is to be considered as a true proteid, it is evidently either an albumin, a combination of an albumin with a proteose, or a proteose. We have seen that those fractional precipitates which consist largely or wholly of proteose have little or no diastatic action, amylolytic power being manifested most strongly in the fractions containing the most albumin, and least in those containing but little, though not in strict proportion to the amount of the albumin. It is to be concluded that the diastatic enzyme is most closely related to the albumin, named leucosin, and it is not improbable that further careful study will show more clearly what this relation is.

## NOTE ON THE PURIFICATION OF GLUCINUM SALTS.<sup>1</sup>

BY EDWARD HART.

Received January 19, 1895.

**T**WENTY years ago I found glucinum in a clay brought to Dr. Drown's private laboratory, in Philadelphia, for analysis. The experience gained then in making the separation from alumina showed clearly that none of the methods then known gave a satisfactory separation. In dissolving the carbonate we found that alumina also dissolves, and that in treating the oxides with solution of ammonium chloride, alumina as well as glucina dissolves.

In beginning the purification of glucina from beryl, which I have undertaken for a more careful study of the metal and its alloys, I determined, if possible, to prepare it in some other way than by the use of the time-honored ammonium carbonate method which, besides giving a material of doubtful purity, is expensive and tedious. Such a method has been found based on the properties of the mixed sulphates from beryl, and which seems not to have been used for this purpose. Perhaps it will be best to describe the method now used in full, without describing the failures through which the work passed.

The powdered beryl is first fused with mixed carbonates and then ground and washed with water. The powdered mass is then mixed with sulphuric acid and evaporated to make the silica insoluble. The sulphate solution obtained from this material is evaporated and treated with an excess of potassium sulphate. Alum crystallizes out and is purified by recrystallization. The mother-liquor contains the glucinum along with the iron and alkaline sulphates. Potassium chlorate is added in excess, and the solution heated to peroxidize the iron. Sodium carbonate solution is now added, little by little, the solution being boiled after each addition until a filtered sample shows no yellow color. The whole solution is then filtered, and the glucinum which will be contained in the filtrate is precipitated by further addition of sodium carbonate.

<sup>1</sup> Read at the Boston Meeting, December 28, 1894.



The method, of course, depends upon the fact that it is impossible to throw down the glucinum until the greater part of the acid has been saturated, the glucinum remaining in solution as basic sulphate. Iron and aluminum, on the contrary, are easily separated. Some care is needed in order to get rid of the last trace of iron, which persistently remains in solution until the point at which the precipitation of glucinum begins is almost reached.

A sample prepared in this way was perfectly soluble in hydrochloric acid, gave no reaction for iron with potassium ferrocyanide, was completely soluble in an excess of ammonium carbonate and caustic potash. The ammonium carbonate solution gave no precipitate on the addition of ammonium oxalate. The method is exceedingly simple, convenient and cheap, and leaves nothing to be desired.

---

## THE COMPOSITION OF THE TUBERCULOSIS AND GLANDERS BACILLI.

BY E. A. DE SCHWEINITZ AND MARION DORSET.

Received April 30, 1895.

WHILE many examinations of the products of bacilli have been made during the past years comparatively little attention has been paid to a comparison of the proximate and ultimate analyses of the germs themselves that are morphologically different, and produce different pathological changes.

Cramer<sup>1</sup> gives the results and analyses of cholera germs from different sources, and concludes that upon easily assimilable media the composition of the bodies of the same germ from different sources, and which vary in virulence, is about the same. Where, however, the media supply food that is but difficultly assimilable the composition of the bodies of the germs will vary. The comparison which he makes between these and several other species shows a variation which indicates a distinct and characteristic composition for each germ.

We have had occasion to collect large quantities of the tuberculosis and glanders bacilli, and have submitted the germs, grown both on the ordinary glycerol beef broth and on artificial

<sup>1</sup> *Arch. f. Hygiene*, 16.

media, to proximate and ultimate analyses. The results are presented in tabulated form.

The germs were freed by filtration from the culture liquid and the last traces of the soluble products removed by washing either with water alone or with the addition of sodium carbonate. The germs were then dried over sulphuric acid and, just before analysis, were further dried at 100° C. In drying, the germs underwent but slight change of color if they had been thoroughly washed. The analyses were made with the germs obtained from one and the same original culture, but the growths of eight or ten different generations were mixed together to secure an average sample. The artificial media used for the cultivation of the tuberculosis bacillus had the following composition:

Water.....	1,000 cc.
Glycerol.....	70 grams.
Acid potassium phosphate.....	1 gram.
Ammonium phosphate.....	10 grams.
Sodium chloride.....	10 "
Asparagin.....	2 "
Magnesium sulphate.....	0.2 gram.

In table I are given the determinations of the carbon, hydrogen, nitrogen, phosphorus, sulphur, ash, in column I, calculated upon the weight of the sample dried at 100° C.; in column II, upon the ash free substance. With the exception of the nitrogen there seems to be but little variation in the composition of the germs grown on beef broth or on artificial culture media:

I. TABLE GIVING ELEMENTARY ANALYSES OF BACILLUS TUBERCULOSIS.

	Beef broth.		Beef broth.		Beef broth.		Artificial media.	
	Per cent.		Per cent.		Per cent.		Per cent.	
	I.	II.	I.	II.	I.	II.	I.	II.
Carbon.....	...	...	60.12	62.61	62.98	64.06	62.16	63.35
Hydrogen.....	9.22	9.60	9.15	9.53	7.39	7.52	9.19	9.36
Nitrogen.....	7.34	7.64	7.27	7.40	8.04	8.18	8.94	9.14
Sulphur.....	0.44	0.45	....	....	....	....	0.22	0.23
Phosphorus soluble in dilute nitric acid... }	0.66	....	0.19	....	....	....	....	....
Phosphorus, total (Carius).. }	0.77	....	0.83	....	0.87	....	0.66	....
Ash.....	4.03	....	4.03	....	1.77	....	1.92	....

Table II gives the elementary analyses of the bacillus of glanders. The germs for these analyses were filtered off, washed a number of times with water and cold absolute alcohol and dried.

A comparison of these results with those of the bacillus of tuberculosis shows a great and distinctive variation.

II. TABLE GIVING ELEMENTARY ANALYSES OF BACILLUS MALLEI.

	Beef broth.	
	Per cent.	
	I.	II.
Carbon .....	41.81	44.89
Hydrogen .....	5.89	6.20
Nitrogen .....	14.05	14.81
Sulphur .....	0.99	1.04
Phosphorus, total (Carius).....	1.10	....
Ash .....	5.18	....

The variations in the composition of these two bacilli is still more apparent in a comparison of the amount of the proximate constituents as shown in tables III, IV, V, and VI. The determinations were made according to the general methods prescribed for such analyses. The nitrogen determinations were made by the Kjeldahl method, and from these results the albuminoids were calculated. The figures reported in the table as cellulose were obtained by treating the residue from the alcohol extract with 1.25 per cent. caustic soda for forty to sixty minutes, washing well, then digesting the residue with 1.25 per cent. sulphuric acid for the same length of time, washing, and drying. The loss by ignition of the dried residue should indicate cellulose.

The presence of cellulose in the organs of tuberculous individuals has been examined by Freund, Dreyfuss, Toyosaku Nishimura, with somewhat discordant results. Freund (*Jahr. d. g. Wiener Aerzte*, 28, 1886) treated the organs and blood from twenty-five different cases, first by extracting with ether and alcohol, then with dilute sulphuric acid. In this way there were left behind hard round lumps about the size of tubercles, which, while insoluble in dilute were soluble in strong sulphuric acid. This solution diluted with water and heated gave the reduction test for sugar.

III. *BACILLUS TUBERCULOSIS. Beef Broth 1.*

	1.		2.		Average.	
	Per cent.		Per cent.		Per cent.	
	I.	II.	I.	II.	I.	II.
Ether extract.....	39.64	41.29	38.95	40.32	39.29	40.80
Alcohol extract .....	....	....	....	....	....	....
Albuminoids.....	45.81	47.31	45.87	47.85	45.84	47.53
Cellulose .....	6.95	7.24	....	....	6.95	7.24
Ash.....	4.12	....	3.94	....	4.03	....

IV. *BACILLUS TUBERCULOSIS. Beef Broth 2.*

	1.		2.		Average.	
	Per cent.		Per cent.		Per cent.	
	I.	II.	I.	II.	I.	II.
Ether extract .....	....	....	....	....	....	....
Alcohol extract .....	3.04	3.10	....	....	3.04	3.10
Albuminoids.....	50.25	51.12	45.43	46.25	47.84	48.68
Cellulose .....	7.37	7.68	....	....	7.37	7.68
Ash.....	1.67	....	1.87	....	1.77	....

V. *BACILLUS TUBERCULOSIS. Artificial Media.*

	1.		2.		Average.	
	Per cent.		Per cent.		Per cent.	
	I.	II.	I.	II.	I.	II.
Ether extract.....	37.76	37.88	37.98	38.71	37.57	38.34
Alcohol extract .....	4.69	4.79	4.19	4.28	4.44	4.53
Albuminoids.....	55.87	57.12	....	....	55.87	57.12
Cellulose .....	3.82	3.89	5.69	5.80	4.75	4.84
Ash.....	1.92	....	....	....	1.92	....

VI. *BACILLUS MALLEI. Beef Broth.*

	1.		2.		Average.	
	Per cent.		Per cent.		Per cent.	
	I.	II.	I.	II.	I.	II.
Ether extract.....	7.91	8.26	7.67	8.09	7.78	8.17
Alcohol extract.....	....	....	....	....	....	....
Albuminoids.....	89.81	94.68	85.71	90.43	87.76	92.55
Cellulose .....	5.87	6.19	....	....	5.87	6.19
Ash.....	5.18	....	....	....	5.18	....

Schulze's method was also used. Lungs, spleen, peritoneum, and dried blood were cut up finely and subjected to the action of nitric acid and potassium chlorate, white, round nodules, or a flocculent substance were left behind, which, submitted to analysis, after solution in cupric ammonia and reprecipitation, gave results corresponding to cellulose.

Nishimura<sup>1</sup> used for experiment the lungs and blood of tuberculous cows and also of men. The organs, after being finely divided were extracted with ether and alcohol and then with two per cent. sulphuric acid.

The residue, when treated with strong sulphuric acid, gave a solution that yielded the Trommer sugar test only twice out of six experiments.

Nishimura then tried the alkali method. The material was fused with potassium hydrate in the oil-bath at 180° C., the fusion acidified with sulphuric acid, then made slightly alkaline and allowed to stand until clear. The residue was filtered off and tested for cellulose. By this method, from the lungs of a grown person a slight reaction for cellulose resulted with Trommer's test. The spleen and liver, treated in the same way also indicated cellulose. In two cases from children, lungs, liver, and spleen gave the cellulose test.

How should this cellulose content be present in the organs? The most plausible supposition is the assumption that this comes from the presence of the bacilli themselves, and that the bodies of the latter are rich in cellulose. Upon this assumption Dreyfuss<sup>2</sup> examined several varieties of bacilli, *bacillus subtilis*, *pus bacillus*, *aspergillus glaucus*, and by the fusion method with caustic potash, succeeded in obtaining the reduction and phenylhydrazine tests.

Nishimura, found, however, that other bacilli, *e. g.*, the water bacillus No. 28, did not show the presence of cellulose. He extended his researches to the tubercle bacilli themselves. He made four tests upon the tubercle bacilli from glycerol bouillon cultures using the alkali method, but obtained no reduction. From this he concludes that cellulose is not present in the tubercle bacilli.

In our examination of the tubercle bacilli, as indicated above, the digestion of the residue, after extraction with ten per cent. sulphuric acid gave distinct reduction tests with Fehling's solution. In two experiments Hoppe-Seyler's method, by fusing with caustic potash at 180°, was used. In the one a good reduction test was obtained; in the other the reduction test failed.

<sup>1</sup> *Arch. f. Hygiene*, 21, [1], 52.

<sup>2</sup> *Ztschr. Physiol. Chem.*, 18, [3, 4], 367.

From these tests we would conclude that cellulose is present in the tubercle bacilli, but in very minute amount, which may, in some instances, escape detection by the methods generally adopted. Nishimura thinks that possibly the tubercle bacilli form cellulose when they grow in the body, but not on artificial culture media. The fact, however, that the analyses indicated cellulose, both when grown upon glycerol beef broth and upon the mineral salt cultures, would make it probable that the cellulose is a normal constituent and can be produced by the germ from whatever material it feeds upon.

The proximate analyses of the glanders bacilli show results which are markedly different from those obtained with the tubercle bacilli. While the determination of cellulose by the method of difference would indicate its presence, the fusion with caustic potash, according to the same method adopted for the tubercle germs, and subsequent treatment with sulphuric acid indicates the absence of cellulose. Care was taken in filtering the tuberculosis and glandery germs that they were not contaminated with cellulose from filter-paper. The most of them were filtered through porcelain and then scraped off.

In order to show more clearly the variation in the body composition of different germs the following table is appended which gives results obtained by Cramer and others, with different germs, upon varying media. The change in the nitrogen content is very marked, and while the difference of medium influences this to some extent there is still sufficient variation in the different germs to permit of a possible distinction of species. While the products of germs are invaluable as an aid to identification it would appear that the chemical study of the bodies of the germs and the differences in their proximate constituents, especially albuminoids and fat, and a more distinctive study of the albuminoids might be very useful in aiding classification.

In order to form some idea of the composition of the fat extracted from the tuberculosis and glanders bacilli, the fats were saponified with caustic soda and the fatty acid separated. The quantity of acids obtained, however, was small and it was only possible to make melting-point determinations. From these the acids of the glanders seemed to be oleic and palmitic, those from the tubercle bacilli, palmitic and arachidic acid.

The difference in the fatty acids apparent in these two, and which would probably vary as much in other germs, could doubtless be made of use in classification. This study is being continued further and extended to the hog cholera, swine plague, and allied germs.

Media	Albuminoids per cent.			Ether and alco- hol extract per cent.		Ash per cent.	
	1 per cent Peptone agar.	2 per cent Peptone agar.	1 per cent Soda.	5 per cent Peptone agar.	1 per cent Soda.	5 per cent Peptone agar.	1 per cent Peptone agar.
	Bacilli.			Nitrogen.			
Pfeiffer's capsule bacillus .....	66.6	70.0	....	14.06	....	9.10	....
Pneumonia bacil- lus .....	71.7	79.8	....	11.3	....	10.36	....
Bacillus of Rhi- noscleroma ....	68.42	76.2	....	9.1	....	9.33	....
Spirillum of chol- era .....	....	64.96	....	....	....	...	30.78
No. 28.....	73.1	79.6	....	17.08	....	7.79	....
	7 per cent Glycerol beef broth. per cent	7 per cent Artifi- cial media. per cent	5 per cent Glycerol beef broth. per cent	1 per cent Peptone beef broth. per cent	Car- bon. per cent	Hydro- gen. per cent	Ash. per cent
Tuberculosis ....	7.34	8.94	....	....	62.98	7.34	1.77
Glanders .....	....	....	14.05	....	41.89	5.89	5.18
Swine plague ...	....	....	....	11.81	44.57	7.20	12.41

BIOCHEMIC LABORATORY,  
BUREAU OF ANIMAL INDUSTRY.

## A CONVENIENT FORM OF UNIVERSAL HAND-CLAMP.<sup>1</sup>

By PETER T. AUSTEN AND W. A. HORTON.

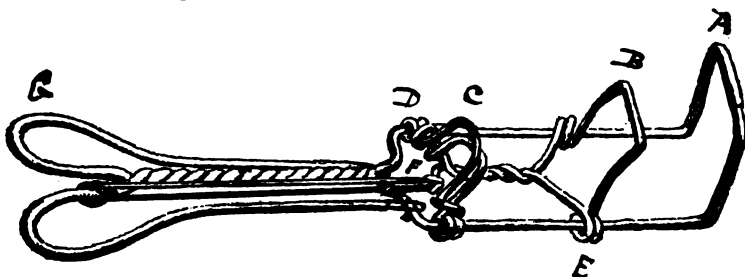
Received April 23, 1895.

THE various holders and hand-clamps used for holding test-tubes and smaller forms belong, as a rule, to two classes. The bite is effected either by a spring or by a pressure exerted by the hand. The difficulty with the first class of holders is that the spring is often inconveniently strong for delicate tubes, and not strong enough for flasks. The second class often fails when long continued holding is involved, as muscular pressure relaxes after a time.

The following little device was worked out to afford a con-

<sup>1</sup> Read before the New York Section, December, 1893.

venient holder that should take from nothing up to a diameter of an inch and a half and yet allow a grasp which corresponds to the weight of the object held, and also not tire the hand, no matter how long it is held.



The clutch B slides on the parallel bars E, and is slightly smaller than the counter-clutch A. This, with its curvature, allows it to grasp any object, no matter how small, that is placed between B and A. A double bearing, to insure ease of movement, is effected by winding the wire at D. The double arch C allows the thumb to press easily and comfortably against it, and act as a knee-joint. The swell G keeps the handle in the grasp, and the rubber strap F brings the traveling clutch back and opens the clamp as soon as the pressure is removed from C.

To use the apparatus, the handle is securely grasped and the end of the thumb is placed against C. On straightening the thumb, in the manner of a knee-joint, the object is tightly held between the clutches. The hand does not tire on continued holding because the pressure is taken in a straight line on the bones of the thumb, and hence calls for so slight a muscular action as to be practically inappreciable.

The clamp is manufactured by Richards and Company.

CHEMICAL LABORATORY OF THE BROOKLYN  
POLYTECHNIC INSTITUTE.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF  
CHEMISTRY. No. 1.]

### ELECTROLYTIC SEPARATIONS.

BY EDGAR F. SMITH AND DANIEL L. WALLACE.

Received April 22, 1895.

COMMUNICATIONS relating to the electrolytic separation of metals, present in solution as double cyanides, have appeared, from time to time, in this Journal and in other pub-



lications devoted to chemistry, during the past seven years. Thus it was found that in solutions, such as that mentioned, it was possible to separate *cadmium* from zinc, arsenic, tungsten, molybdenum, osmium, nickel, and cobalt; *mercury* from copper, zinc, nickel, cobalt, palladium, arsenic, tungsten, molybdenum, platinum, and osmium; *gold* from palladium, platinum, copper, cobalt, zinc, and nickel; and *silver* from copper, zinc, nickel, cobalt, arsenic, tungsten, molybdenum, platinum, and osmium. No difficulties were encountered in these separations. About the only objection that could be presented against them, and one that would in any manner postpone their immediate adoption into general analysis, was the fact that from twelve to fourteen hours were required for the deposition of the cadmium, mercury, gold, and silver.

Not more than a year ago Smith and Spencer (This Journal, 16, 420) observed that the deposition of both mercury and silver was markedly accelerated when the electrolyte undergoing decomposition was heated from 65° to 70° C. It will be recalled that all the earlier separations noted above had been carried out at the ordinary temperature. It appeared, therefore, desirable to further extend the study, and in the lines which follow results are given which were obtained from this new point of view.

While cadmium can be completely separated from its double cyanide solution *in the cold*, the reverse occurs if the liquid be raised to 65°. Thus, in the communication of Smith and Spencer, evidence is given that in a warm solution silver can be fully separated from cadmium, and in the table below it will be observed that mercury and cadmium can be similarly separated. It was, therefore, impossible to review the separations of cadmium from the various metals from which it had been fully separated in the cold. The experiments were accordingly limited to mercury, gold, and silver with several typical metals, as the conditions under which their separation proved successful would doubtless serve for the remaining representatives of the various groups from which separations had been effected.

In the earlier communications it was customary to report the strength of the acting current in cubic centimeters of electrolytic gas per minute. In the present presentation the *normal density* (N. D.) of the current for 100 square centimeters of electrode

surface will be given in ampere units. The reader will also bear in mind that the temperature of the solutions operated upon was, in all cases, 65° C.

## MERCURY SEPARATIONS.

Mercury taken. Grams.	Mercury found. Grams.	N. D. of current in ampere units per minute.	Time required for precipitation.	Potassium cyanide in grams.	Cadmium present in grams. per cent.	Zinc present in grams. per cent.	Nickel present in grams. per cent.	Cobalt present in grams. per cent.
0.1901	0.1907	0.02	3 hours.	2	100	100	100	100
.....	0.1903	0.02	3 "	2	100	...	...	...
.....	0.1902	0.06	3½ "	2	...	100	...	...
.....	0.1900	0.06	3½ "	2	...	100	...	..
.....	0.1896	0.06	3½ "	2	...	100	...	...
.....	0.1905	0.08	3½ "	3	...	...	100	...
.....	0.1908	0.08	3½ "	3	...	...	100	...
.....	0.1898	0.08	3½ "	2	...	...	...	100
.....	0.1896	0.08	3½ "	2	...	...	...	100

In ordinary gravimetric analysis it would not be possible for the analyst to separate mercury from any one of the metals just given as completely nor as quickly as indicated in the table.

Gold was separated from cobalt, arsenic, copper, zinc, and nickel, the quantity of gold present in each trial being 0.1087 gram, and each of the other metals in equal amount. But one separation was made with each metal. The quantity of cyanide ranged from one to two grams; the period required for the precipitation of the gold varied from three to three and one-half hours. In all the trials, excepting that with copper, the current was N. D.<sub>100</sub> = 0.1 ampere. In the exceptional case it was reduced to 0.07 ampere. The quantities of gold obtained were:

1.....	0.1084 gram.
2.....	0.1080 "
3.....	0.1093 "
4.....	0.1088 "
5.....	0.1082 "

The separations of silver were limited to zinc, nickel, and cobalt. The quantity of silver was 0.1465 gram and the other metals in equal amount. The quantity of cyanide in all instances was two grams, while the current strength was N. D.<sub>100</sub> = 0.04 ampere. The time of deposition did not exceed three hours. The precipitated silver equaled:

1.....	0.1464 gram.
2.....	0.1464    "
3.....	0.1460    "
4.....	0.1464    "

The separation of silver from copper and from cadmium is just as rapid and complete as these last separations.

The deposits of mercury, gold, and silver, were carefully examined in the quantitative way for the various metals with which they had been associated; in every instance they showed themselves perfectly pure, so that these methods can be relied upon and trusted where accurate and rapid work is required.

The metallic deposits were washed and dried in the manner described in previous articles.

During the progress of the preceding experiments behaviors were observed pointing toward the separation of silver from gold, and mercury from gold and from silver in cyanide solution, but thus far expectations in these directions have not been realized. When conditions apparently favorable were obtained, traces of one or the other metal would be discovered in the metallic deposit, so that, at this moment, trustworthy and definite data cannot be given.

UNIVERSITY OF PENNSYLVANIA.

## ON THE VAPOR-TENSIONS OF MIXTURES OF VOLATILE LIQUIDS.

BY C. E. LINDBARGER.

Received May 3, 1895.

### CONTENTS.

1. Introductory.
2. Historical.
3. Description of apparatus.
4. Calculation of results.
5. Discussion of sources of error in apparatus.
6. Comparison of the vapor-tensions obtained by the method herein described and those obtained by other methods.
7. Choice and purification of liquids.
8. Preparation of the mixtures.
9. Experimental results with mixtures of normal liquids.
10. Influence of temperature on the vapor-tensions of mixtures of liquids.
11. Relations between the vapor-tensions, partial and total, and the concentrations of the liquid phases.

12. Relations between the concentrations in the gaseous and liquid phases.
13. Heat of dilution and solution; ideal concentrated solutions.
14. The vapor-tensions of mixtures of acetic acid with benzene and with toluene.
15. The molecular mass of liquid acetic acid and a general method of determining the molecular masses of liquids.
16. Résumé.

## I. INTRODUCTORY.

THE investigation of the elastic forces or tensions of vapors emitted by a solution of a fixed substance in a volatile liquid has received much attention, especially within recent years. The impetus for investigations of this kind is, in a great measure, due to the new notions that have been introduced into science in regard to the nature of solutions. The possibility of ascertaining the molecular mass of a substance from a determination of the amount of the depression of the vapor-tension of a liquid, occasioned by its being dissolved therein in known proportions, has induced chemists to study carefully this field of scientific inquiry, which it may truly be said, has been gone over very elaborately.

In the greater part of the work that has been done, both theoretical and experimental, it has been assumed that the dissolved substance is not appreciably present in the gaseous state, and but sparingly present in the liquid state; in other words, the dissolved substance is supposed to be involatile, and the solutions are made dilute.

Now, absolute involatility in any body whatsoever cannot be affirmed; there must always be, at every temperature, some degree of power of assuming the gaseous state, although it may be so slight as to be imperceptible to our senses. Still, for all practical purposes, the assumption of non-volatility in many substances can be admitted, as our means of experimentation are not sufficiently delicate to detect any small amount of volatility.

Although so much has been done on the vapor-tensions of solutions of fixed substances in volatile liquids, comparatively little attention has been paid to the study of the vapor-tensions of mixtures of the volatile liquids; yet this is the general case, of which the restriction that the dissolved substance be fixed

makes only a special application. It must, indeed, be allowed that the consideration of a mixture of vapors, instead of a single one, introduces certain complications into the problem; and this is, perhaps, just the reason so little work has been done on this part of the subject; still difficulties of this sort are probably not unsurmountable.

The limitations of work on vapor-tensions to dilute or, at most, moderately concentrated solutions cannot be said to be satisfactory. True, the theory of solutions has been developed on the hypothesis that dissolved matter, in analogy with gaseous matter, is in a state of considerable dilution; and experimental confirmations of theoretical predictions can be expected only when such a state of affairs is realized. Notwithstanding that circumstance, it seems of importance to extend our line of operations and attack the problems presented by concentrated solutions; perhaps they will be found to exhibit fewer anomalies than has been supposed.

There are two circumstances which render work that has hitherto been done on the vapor-tensions of mixtures of volatile liquids of all concentrations unsatisfactory; they are to be found in the choice of the liquids investigated, and the kinds of vapor-tension measured. The liquids chosen were almost invariably those which are now recognized to be made up of associated molecules; they are just those which exhibit the greatest abnormalities in respect to most of their properties, and it cannot be expected that simple relations, if they exist at all, will be discovered when such liquids are used as material of investigation. All investigators also, almost without exception, have measured only the total pressure of the mixtures of liquids examined, which is the sum of the partial pressures, these, however, being entirely unknown. But more important is it to know the share which each vapor has in the exerting of the total pressure, and only when this is learned can our knowledge of the matter be said to be in any adequate measure complete.

This paper seeks to fill in some degree this gap in the subject of vapor-tensions. The method employed is such as to permit of the specification of the partial pressures of a mixture's components, and also of their concentrations in the gaseous phase. The

choice of the liquids has been made with an eye towards employing those which have been found to be most "normal," so that in the examination of more complex liquids, that is, those consisting of associated molecules, the simplicity to be expected in the phenomena of the former may aid us in getting some light on the possible intricacies of the latter. All the mixtures examined are freely soluble in one another so that no disturbing influence from layer-formation can take place.

In reality, we have before us a case of equilibrium; the equilibrating system consists of two substances, each present in two phases, the liquid and gaseous. We have to ascertain at the points of equilibrium the temperature, the partial pressures of the two substances in gaseous phase, and their concentration in both liquid and gaseous phase.

## 2. HISTORICAL.

The first paper that I know of which treats of the vapor-tensions of mixtures of liquids soluble in every proportion in one another is by Gustav Magnus,<sup>1</sup> who states that, when to a volatile liquid, such as ether, contained in a barometric vacuum, another less volatile liquid, such as alcohol, be added, the tension of the vapors of both liquids is less than that of the ether alone; the cause of this behavior Magnus seeks in a certain reciprocal attraction on the part of the two liquids. Magnus' paper, being almost the first on the subject, contains, as, indeed, is generally the case with pioneer papers, some important statements, which, through the labors of later investigators, have become generalized into wide-reaching laws; but everything in it is purely of a qualitative nature, no reliable quantitative data being given.

Regnault<sup>2</sup> in the course of his extended investigations on the elastic forces of the vapors given off by liquids, determined at

<sup>1</sup> Ueber das Sieden von Gemengen zweier Flüssigkeiten und ueber das Stossen solcher Gemenge. *Ann. der Phys. u. Chem. Pogg.*, 38, 481-492. 1836.

<sup>2</sup> Ueber die Elasticitätskräfte der Dämpfe bei verschiedenen Temperaturen im Vacuo und in Gasen; und ueber die Spannung der Dämpfe aus gemengten oder geschichteten Flüssigkeiten; *Ann. der Phys. u. Chem. Pogg.*, 93, 537-579, 1854, and *Mémoires de l'Académie des Sciences*, 26, 1862. Quatrième Partie: Forces Élastiques des Vapeurs qui sont Émises par les Liquids volatiles, Mélangées par Dissolution reciproque ou superposés. Troisième Classes: Mélanges binaires des Liquides qui se dissolvent mutuellement en toutes Proportions, 724 and 743.

different temperatures by the static as well as dynamic method, the vapor-tensions of several mixtures of various liquids. Regnault did not pay much attention to the composition and analysis of the mixtures investigated, his object being merely to get a general idea of the relations of the vapor-tensions of the mixtures to those of the component liquids. Still there is but a little doubt that the composition of the mixtures is specified with sufficient accuracy to admit of his data being regarded as reliable enough for theoretical considerations and confirmations. In a later section are given his results so rearranged as to furnish some indications of the nature of the phenomenon which they represent. Regnault states in the papers printed in the *Mémoires de l'Académie* that his experiments lead to the same conclusions as those of Magnus; but in the German translation (*loc. cit.*) from the *Comptes rendus*, he does not seem to have given Magnus this credit, which induced the latter in a paper<sup>1</sup> immediately following that by Regnault, to call attention to his results published some eighteen years before (*loc. cit.*). In this last paper by Magnus nothing new is communicated, a considerable part of it being occupied with quotations from his former paper.

Plücker<sup>2</sup> determined by means of Geissler's "Vaporimeter" the composition of the liquid and gaseous phases, as well as the total pressure of the latter, of a system consisting of a mixture of alcohol and water; the work has the stamp of having been done with great care, and the accuracy of the results—rather meager, it must be said—can probably be relied upon.

Bussy and Buignet<sup>3</sup> in the course of their researches on the physical properties of mixtures of hydrocyanic acid and water, made determinations according to the static method of the vapor-tensions of seven mixtures of the above two liquids (page 245 of their memoir). The work, which was carried out at 13.25° is fairly accurate, but the range of concentrations is not extensive enough to permit of utilization of their results.

<sup>1</sup> Ueber die Spannkraft der Dämpfe von Mischungen zweier Flüssigkeiten; *Ann. der Phys. u. Chem. Pogg.*, 93, 579-582, 1852.

<sup>2</sup> Untersuchungen über Dämpfe und Dämpfgemenge; *Ann. der Phys. u. Chem. Pogg.*, 92, 193-220, 1851: A continuation of this article was promised by the author, but I have been unable to find it and regard its appearance as very doubtful.

<sup>3</sup> Recherches sur l'acide cyanhydrique: *Ann. Chim. Phys.*, [4] 3, 231-263, 1864.

While the preceding scientists for the most part endeavored to find relations between the tensions of vapors emitted by a mixture, and those given off by its components in a state of purity, Duclaux<sup>1</sup> set himself about to get a knowledge of the relations of the composition of the liquid mixture to that of the vapors emitted. His method consisted in distilling a large quantity (1100 cc.) of a mixture of known composition and collecting several distillates, the composition of which was determined through their surface tensions by means of the "Drop-method." Duclaux, believing, for reasons which he does not state, that simpler relations are to be discovered, if the proportions of the liquids in a mixture be expressed in volumes rather than in weights, communicates results and data, which, as he neglects to give any accurate indications as to the temperature at which and the pressure under which the mixtures investigated by him entered into ebullition, and as to the amount and direction of the change of temperature as the boiling proceeded, it is impossible to put into a shape permitting of comparison with others; the mixtures studied consisted of water and the series of alcohols up to caprylic alcohol, and of water with formic, acetic, and butyric acids.

Wüllner<sup>2</sup> determined according to the static method<sup>3</sup> the vapor-tension of five different mixtures of ethyl alcohol and water at temperature intervals of about 10° from 11.8° to 84.6°; also of two mixtures of sulphuric ether and alcohol at temperature intervals of about 3° from 7.2° to a little over 30°. Wüllner had especially in mind in his work the determination of the variation of constancy of the ratio of the tension of the mixture of vapors to the sums of the tensions of each vapor alone with the temperature; no mention is made of experimental details and of the purity of the liquids experimented upon.

It may be well for the sake of completeness to make mention

<sup>1</sup> Sur les Forces Élastiques Émises par les Mélanges de deux Liquides: *Ann. Chim. Phys.*, [5] 24, 305-345. 1878.

<sup>2</sup> "Ueber die Spannkraft der Dämpfe von Flüssigkeitsgemischen": *Ann. der Phys. u. Chem. Pogg.*, 129, 353-366. 1866.

<sup>3</sup> *Ann. der Phys. u. Chem. Pogg.*, 103, 534-542.



here of Alluard's,<sup>1</sup> Berthelot's,<sup>2</sup> and Brown's<sup>3</sup> work on the boiling points of mixtures of liquids, although little is to be found therein which bears directly upon our subject.

An important experimental as well as theoretical investigation on the subject in question has been made by Konowalow.<sup>4</sup> The method employed was the static, so arranged, however, that the error arising from the change of composition of a liquid mixture due to the evaporation of its components was reduced to a minimum. The determinations were made with mixtures of water with each of the first four members of the series of alcohols,  $C_nH_{2n+2}O$ , and of the series of acids  $C_nH_{2n+2}O_2$ , at several different temperatures; the work of Konowalow may be looked upon as very accurate.

Among Raoult's numerous and important publications on the vapor-tensions of solutions, there is one which deserves mention in the history of the vapor-tensions of mixtures of volatile liquids, even if one component of the binary mixtures investigated by him has but a feeble tension of vapor. The paper referred to<sup>5</sup> treats of the vapor-tensions of solutions of turpentine, nitrobenzene, aniline, methyl salicylate, and ethyl benzoate, all almost non-volatile liquids, in ether; the determinations were made at ordinary temperatures by the static method, and are to be considered as remarkably exact. In a later section, the data will be given in a modified form.

In the last five or six years papers by Planck, by LeChatelier, and by Nernst, treating of the theoretical side of the question, have appeared; from their importance as well as for convenience of reference, their contents will be quite fully reproduced.

Max Planck<sup>6</sup> enunciated certain relations between the differ-

<sup>1</sup> "Experiences sur la Temperature d' Ebullition de quelques Mélanges binaires de Liquides que se dissolvent mutuellement en tous Proportions." *Ann. Chim. Phys.*, [4] 1, 384-392, 1894.

<sup>2</sup> "Sur la Distillation des Liquides Mélanges." *Compt. rend.*, 57, 430 (1863); *Ann. Chim. Phys.*, [4] 1, 384-392, 1864.

<sup>3</sup> "On the Distillation of Mixtures of Carbon Disulphide and Carbon Tetrachloride." *Transactions of the Chemical Society of London*, 39, 304, 1887.

<sup>4</sup> "Ueber die Dampfspannungen der Flüssigkeitsgemischen." *Ann. der Phys. Weid.*, 14, 219, 1881.

<sup>5</sup> "Ueber die Dampfdrucke Atherischer Lösungen." *Ztschr. phys. Chem.*, 2, 353-373, 1888.

<sup>6</sup> "Ueber die Dampfspannung von verdünnten Lösungen flüchtiger Stoffe." *Ztschr. phys. Chem.*, 2, 405-414, 1888.

ence of concentrations of mixtures of two volatile substances in equilibrating gaseous and liquid phases, and the depression of the vapor-tension, which permit of experimental verification. Planck assumes the applicability of the law of Raoult-van't Hoff and that of Henry to the case of the vapor-tensions of mixtures of volatile substances (liquids); that is, there must be direct proportionality between lowering of vapor-tension and molecular concentration, and also between concentration in liquid phase and partial pressure in gaseous phase; furthermore he states expressly that his deductions are made for the case of dilute solutions only, and that the substances in all phases of a system consist of normal molecules.

Such a system made up of a liquid and gaseous mixture in contact may be represented by the symbol:

$$nm, n_1m_1 + n'm', n'_1m'_1,$$

where  $n$  and  $n_1$  represent numbers of molecules, and  $m$  and  $m_1$  molecular masses; the accented letters refer to the vapor, and the unaccented to the liquid; those written with the subscript have reference to the dissolved substance, those without subscript to the solvent;  $n$  and  $n'$  are large in comparison with  $n_1$  and  $n'_1$ . The numerical concentrations of the individual substances are:

$$c = \frac{n}{n+n_1}; c_1 = \frac{n_1}{n+n_1}; c' = \frac{n'}{n'+n'_1}; c'_1 = \frac{n'_1}{n'+n'_1}.$$

If a reaction supervenes occasioning the following changes in the numbers of the molecules:

$$\delta n : \delta n_1 : \delta n' : \delta n'_1 = \gamma : \gamma_1 : \gamma' : \gamma'_1,$$

equilibrium occurs, in case this condition,

$$\gamma \log c + \gamma_1 \log c_1 + \gamma' \log c' + \gamma'_1 \log c'_1 = \log K,$$

is fulfilled<sup>1</sup>;  $K$  is a function of pressure and temperature. In the case before us, we have two different reactions to consider: the vaporization of the solvent and that of the dissolved substance. Accordingly:

$$\begin{array}{llll} 1. & \gamma = -1 & \gamma_1 = 0 & \gamma' = 1 & \gamma'_1 = 0 \\ 2. & \gamma = 0 & \gamma_1 = 1 & \gamma' = 0 & \gamma'_1 = 1 \end{array}$$

The necessary conditions for equilibrium are:

<sup>1</sup> See M. Planck. Ueber die Vermehrung der Entropie. *Ann. der Phys. Wied.*, 32, 489, 1887.)

$$\begin{aligned} -\log c + \log c' &= \log K \\ -\log c_1 + \log c_1' &= \log K_1, \end{aligned}$$

or, if it be taken into consideration that  $c$  and  $c'$  differ but little from unity, and if members of higher degrees be neglected :

$$\begin{aligned} c_1 - c_1' &= \log K, \\ \text{and} \quad \log \frac{c_1'}{c_1} &= \log K_1. \end{aligned}$$

Only the first of these relations can be gotten into a form experimentally verifiable in the present state of our knowledge, and, accordingly, it alone will be treated of in this review.

$K$  is not a directly known function of temperature and pressure, and in order to get its expression in terms of those energy-factors, use must be made of the thermodynamic differential equation :

$$\frac{\delta (\log K)}{\delta p} = -\frac{V}{T}.$$

$V$  being the change of volume occasioned by the reaction at the temperature  $T$ ,  $\log K$  developed in a series according to powers of  $(p-p_0)$  becomes :

$$\log K = \log K_0 + (p-p_0) \left( \frac{\delta \log K}{\delta p} \right) + \dots$$

The subscript  $(.)$  indicates that for  $p$  the value  $p_0$  is to be placed ; on account of the great dilution,  $(p-p_0)$  must be small, and hence all terms in the series can be neglected after the first power. If the term  $\frac{V_0}{T}$  be substituted for the differential quotient, the equation

$$c_1 - c_1' = \log K_0 - (p-p_0) \frac{V_0}{T}$$

is obtained.

$V_0$  is the change of volume of the system, when, at the temperature  $T$  and under the pressure  $p_0$ , a gram molecule of the solvent vaporizes ; accordingly we can put for it the molecular volume of the vapor, which is equal to  $\frac{RT}{p}$  by Boyle's and Gay-Lussac's laws ; we then obtain

$$c_1 - c_1' = \log K_0 - \frac{p-p_0}{p_0}.$$

$K_0$  depends only on the temperature and remains constant during isothermal changes of pressure. If we take  $p=p_0$ , we have to do with the pure solvent, and  $c_1$  and  $c_1'$  must be equal to zero, as well as  $\log K$  also; and generally we may put

$$c_1 - c_1' = \frac{p_0 - p}{p_0}$$

In words this relation runs thus: "The relative depression of the vapor-tension is equal to the difference between the concentrations of the dissolved substance in the liquid and in the vapor."

Planck also got another expression for the differences between the concentrations ( $c_1 - c_1'$ ) in the following manner: If the equation  $c_1 - c_1' = \log K$  be developed in a series according to the powers of  $T - T_0$ , the series

$$\log K = \log K_0 + (T - T_0) \left( \frac{\delta \log K}{\delta T} \right)_0 + \dots$$

is obtained. Treating this equation in a way similar to that taken in the previous case, and making use of the thermodynamic relation,

$$\frac{\delta(\log K)}{\delta T} = \frac{Q}{T^2},$$

we obtain the expression

$$c_1 - c_1' = (T - T_0) \frac{Q}{T_0^2}$$

where  $Q$  is the heat which is derived from the exterior, when a gram-molecule of the solvent vaporizes at the temperature  $T_0$  and under the pressure  $p_0$ . Planck accordingly enunciates this law: "The difference in the concentrations of the dissolved substance in the liquid and in the vapor is equal to the rise in the boiling point, divided by the square of the boiling point and multiplied by the molecular heat of vaporization of the solvent."

From experiments by Konowalow (*loc. cit.*) on mixtures of formic acid and water and of isobutyl alcohol and water, Planck calculated, according to his two formulas just given, the concentration in the gaseous phase, a satisfactory correspondence between the two sets of data being found.

Le Chatelier<sup>1</sup>, in his remarkable paper on chemical equilib-

<sup>1</sup> Recherches Experimentales et Théoriques sur les Equilibres Chimiques: Extrait des Annales des Mines de Mars-Avril, 1888, 281.

rium, devotes a section to the theoretical treatment of the vapor-tension of a mixture of liquids. The expression finally arrived at is quite complicated, and, although important results may be probably obtained by its applications, it is not expedient to enter into its development here.

A. Winkelmann<sup>1</sup>, in seeking experimental proof of the relations established by Planck (*loc. cit.*) between the composition of liquid mixtures and their vapors, condensed some of the vapors arising from a solution and ascertained the composition of the condensed vapors, or liquid by measuring its index of refraction. The experiments were made with mixtures of water and propyl alcohol; there is undoubtedly a correspondence between his experiments and Planck's theory, but it cannot be said to be very close.

Nernst<sup>2</sup> also has found an expression for the concentration of a volatile dissolved substance in the gaseous phase in terms of vapor-tensions. If  $n$  be the number of molecules of dissolved substance contained in  $N$  molecules of a solvent,  $k$  a factor of proportionality corresponding to the absorption coefficient of the dissolved substance, and  $p$  the partial pressure of the vapor of the dissolved substance in the saturated vapors over the solution, by Henry's law, the equation

$$Kp = \frac{n}{n+N}$$

may be formed. The vapor-tension of the solvent  $P$  is

$$P = P_0 \frac{N}{N+n}$$

where  $P_0$  is the vapor-tension of the pure solvent at the temperature in question.

According to Dalton's law, the total pressure of the saturated vapor  $\pi$  of the solution is

$$\pi = P + p$$

<sup>1</sup> Ueber die Zusammensetzung des Dampfes aus Flüssigkeitsgemischen: *Ann. der Phys. Wied.*, 39, 1-15, 1890.

<sup>2</sup> Vertheilung eines Stoffes zwischen zwei Lösungsmittel und zwischen Lösungsmittel und Dampfraum: Dampfspannungen verdünnter Lösungen flüchtiger Stoffe *Ztschr. phys. Chem.*, 8, 124, 1891.

and the composition of the vapor may be shown to be

$$K \frac{n'}{N' + n'} = \frac{p}{P + p}.$$

Where  $N'$  and  $n'$  have the same significance for the vapor as  $N$  and  $n$  have for the liquid mixture.

Nernst gives in a little table a comparison of the data calculated by his formula with those obtained by the use of Planck's formula, both in turn being compared with the results of Winkelmann's experiments.

TABLE I.

*Mixture of 6.2 grams propyl alcohol and 93.8 grams water.*

<i>t</i>	$P_0$	$\pi$	$P$	$p$	$\frac{n'}{N' + n'}$	Per cent alcohol in vapor.		
						Winkelmann.	Nernst.	Planck.
17.65	15.0	20.8	14.7	6.1	0.293	....	58.0	64.2
31.5	31.3	....	30.7	....	....	52.3	59.4	66.0
40.3	55.7	79.4	54.6	24.8	0.312	57.4	60.2	67.2
51.0	96.7	138.7	94.8	43.9	0.316	60.8	61.9	67.7

It is apparent that Nernst's calculated data correspond better with the data observed than do those calculated by Planck's formula, although the correspondence in no case can be reckoned very close; it must be kept in mind, however, that Winkelmann's method is not very exact, and that the vapor-tensions and composition of distillates have been measured on chemical preparations from different sources. A difference, which may be called an advantage, between Nernst's and Planck's formulas, is that the former is not, like the latter, restricted to the consideration of dilute solutions only.

Nernst has also developed certain views in regard to the vapor-tensions of binary mixtures of volatile liquids.<sup>1</sup>

Taking as base of his considerations the empirical law: the vapor-tension of a liquid is lowered when a foreign fixed substance is dissolved in it; he states that this law is applicable also to solutions of volatile substance, only, in this case, the superincumbent vapor consists not of that of the solvent alone, but of a mixture of those of the dissolved liquid and of the solvent; the gaseous phase of the system contains both components of the so-

<sup>1</sup> *Theor. Chem.* 97, 1893, and *Siede und Schmelzpunkt*, 67, 1894.

lution, and according as the partial pressure of one component is greater or less than the diminution of the vapor-tension of the other which it causes by its presence, the total tension of the solution is greater or less. If now a small quantity of a liquid, A, be added to a liquid, B, the vapor-tension of B will be diminished proportionally to the quantity of A added; but the total pressure of the resulting solution will be increased, inasmuch as A as well as B gives off vapors, and the partial pressure of A is so much the greater as the solubility of the vapor A in the solution is smaller. According as the first or the second influence preponderates, the vapor-tension of the solution will be smaller or greater than that of the liquid B in a state of purity. Since the properties of such a mixture must vary continuously with the composition, the influence of the proportions of the two liquids upon the vapor-tension of the mixture may be considered under three cases.

1. The vapors of both A and of B are easily soluble in each other. If we add ever-increasing quantities of A to B the vapor-tension of the mixture will at first sink to a minimum and then rise, until, when a very great quantity of A has been added, it will approximate to that of the liquid A in a state of purity.

2. The vapors of A and of B are but slightly soluble in each other. If constantly increasing quantities of A be added to B, the vapor-tension increases, reaches a maximum, and decreases when a large excess of A has been added, to that of the pure liquid A.

3. The vapor of A is easily soluble in B, while the vapor of B is but slightly soluble in A. The addition of constantly increasing quantities of one liquid to the other causes the vapor-tension of the resultant mixture to pass without maximum or minimum from the vapor-tension of the second liquid to that of the first. But it is perhaps possible that the vapor of B in A is so difficultly soluble that the addition of a small portion of B to A elevates the vapor-tension, while at the same time the vapor of A is so easily soluble in B that by addition of A to B the vapor-tension is lowered. In that case, when B is added to A the vapor-tension increases at first, passes through a maximum, decreases to pass through a minimum, finally rising and approximating, when great excess of B is present, to that of the pure liquid B.

Recently, George U. A. Kahlbaum<sup>1</sup> and his assistants have determined according to the dynamic method the vapor-tensions at different temperatures of mixtures of water with formic and with acetic acid; also of mixtures of various acids of the fatty series. The determinations, which are very numerous, have been made by a method and with material undoubtedly capable of giving the best of results; it is to be regretted, however, that associated, instead of normal, liquids were taken.

It is seen in the foregoing historical sketch that only in the rarest cases have mixtures of normal liquids been investigated as to their vapor-tensions, and the partial pressures of the constituents of the vapor been determined. Now, as already stated on page 617, in order to get a full knowledge of the phenomena of vaporization of mixtures of volatile liquids, we must learn what the partial pressures of each is, when converted into vapor in equilibrium with the liquid phase; and we are the more likely to get clear ideas by investigating the simplest mixtures first, that is, mixtures made up of simple normal molecules. Having by considerations similar to these been led to take normal liquids to form the mixtures, the vapor-tensions of which are to be determined, my first task was to devise some experimental method, which furnishes a means of measuring the partial tensions of the vaporous members of a system of bodies. In order to do this, it is almost indispensable that the composition of the vapor be known, for, that being the case, it is easy to determine what part of the total pressure is to be attributed to each of its components. The problem then reduces itself to one of a simple analysis; but the difficulty is to get the vapor away from the liquid with which it is in equilibrium without its composition becoming changed during the operation. If the so-called static method of determination of vapor-tensions be adopted, it is possible by enlargement of the barometric vacuum to be filled by the vapor, and, after equilibrium has been attained, by separation of the liquid from the vapor by means of a stop-cock or other arrangement, to get enough of vapor to permit of its analysis. But a small amount can be obtained, however, and there is

<sup>1</sup> Studien über Dampfkraftmessungen. Basel, 1893.



great danger that the composition of the liquid mixture becomes considerably changed.

It is possible to collect some of the condensed vapor given off by a boiling mixture of liquids, and determine its composition, as did Duclaux in the paper cited above (page 620). Here, although it is easy to get a sufficient quantity of the condensed mixture of vapor to permit of quite accurate analysis,—provided that a method of analysis of the two liquids in question had been elaborated,—the change of concentration of the solution during the boiling as well as the concurrent change of temperature, together with the other disturbing circumstances, render the accuracy of such work rather illusory.

Accordingly, another means of determination of vapor-tensions had to be found for the purpose of this investigation; and, indeed, the method founded upon the determination of the quantity of a volatile liquid carried off by a definite volume of an inert gas made to pass through it, and the direct subsequent analysis of the gaseous mixture, either by passing it through appropriate liquid absorbents, such as an alkali, where one of the components of the gaseous mixture is an acid, or over decomposing agents, such as red-hot lime, etc., in case one of the components contains sulphur or a halogen, has been adopted; the method, be it said right here, has been found to meet the requirements of the investigation in a satisfactory manner. It is, indeed, true that the variety of the liquids which can be subjected to investigation is limited, for one member of a mixture must needs be a liquid containing a halogen or sulphur atom, or an acid. Still it is possible to find enough such liquids of differing functions that the results obtained by them can without question be transferred to mixtures made up of any normal liquids whatsoever, and any conclusions drawn, become general.

### 3. DESCRIPTION OF APPARATUS.

It is of prime importance in the determination of vapor-tensions that the temperature be kept uniform; accordingly I describe, first of all, the apparatus employed for that purpose.

*Thermostat.*—This consisted of a cylindrical copper vessel holding nearly forty liters of water. It was heated by means of

a ring burner; the pressure of the gas was kept constant by means of a pressure-regulator, and a thermo-regulator as described by Ostwald,<sup>1</sup> controlled the combustion of the gas. To insure uniformity of temperature in all parts of the bath, the water was kept in constant agitation by means of a number of fine streams of air blown up through it, the laboratory being provided with air under pressure. Such a means of agitation gives very satisfactory results; it takes up but very little room, and permits of the examination of the pieces of apparatus plunged in the water by shutting off for a few seconds the flow of the air.

The temperature of the bath remained constant to within  $0.05^{\circ}$  during an experiment; the thermometer employed was one graduated to tenths of degrees, and had recently been tested by the "Physikalische Reichsanstalt" of Berlin.

The apparatus consisted of three principal parts, each made up from material easily found in almost every chemical laboratory. The first part consists of those pieces required to measure a definite volume of air, to compress it enough to force it through the apparatus, and to dry it thoroughly; the second part is the contrivance for saturating the volume of air with the vapor of the liquid under examination; and the third is the arrangement for the analysis of the gaseous mixture.

*First Principal Part of Apparatus.*—This consists of a measuring vessel, a vessel for regulating the internal pressure, a manometer, and a system of drying-tubes. I pass to the description of each.

*The Measuring Vessel* consists of an ordinary bottle of a capacity varying from one to three liters, according as it is required to employ a larger or a smaller volume of air; the height of the bottle should be such that only the neck is above the water; in its neck is fitted a good rubber stopper through which passes one branch of a J tube. This branch of the J tube is made of tubing of about a quarter inch bore, and is about eight inches long, while the other branch has only half this bore, with a length of about three inches. The wider branch of the tube is

<sup>1</sup> *Ztschr. phys. Chem.*, 2, 565, 1888.

pushed through the stopper so that its lower edge is just flush with that of the rubber, and care is taken that this adjustment is in every experiment maintained, as well as that the stopper is always inserted to the same distance in the neck of the measuring vessel. In the upper end of the wider branch of the T tube is inserted (an air-tight joint being assured by the use of rubber tubing) a tube somewhat drawn out and narrowed at its lower end, and provided with a stop-cock at its upper end. The end of the lower part must be about a half inch above level of the stop of the measuring vessel, and the upper end is put, by means of a piece of rubber tubing, in communication with a water supply at constant level about a yard above the thermostat. If the stop-cock be opened, water will flow into the vessel, and displace the air therein contained which escapes through the side branch, which, being in the middle of the vertical branch, is an inch or so above the orifice of the tube introducing the water.

Sufficient mercury is poured into the vessel to make it sit firmly on the floor of the thermostat. The residual volume of the vessel is carefully determined by pouring into it from graduated vessels, enough water to fill it up to the level with the upper surface of the stopper. If the adjustment of the stopper and the tubes be always the same, duplicate determinations of the capacity do not differ by more than one-half cc. If the same volume of mercury always be taken, the volume of water will represent the volume of air passed through a liquid or mixture of liquids undergoing investigation in all determinations.

It is superfluous to make corrections for the expansion of the mercury and the glass when determinations of vapor-tensions are made at higher temperatures, as the error of the estimation of the capacity exceeds the amount of the corrections.

*The Pressure Regulator* consists of a bottle of any convenient size, provided with enough mercury to make it stand steadily under water, and fitted with a twice perforated rubber stopper. Through one of the holes of the stopper passes a tube nearly to the level of the mercury and furnished with a stop-cock at its upper end; this tube is connected by means of rubber tubing with the same water source as the measuring vessel. In the other hole is fitted a T tube, of which one of the horizontal

branches is connected by means of a bit of stout rubber with the narrower branch of the T tube belonging to the measuring vessel, while the other is attached by rubber tubing to the other parts of the apparatus. If water be run into the bottle serving as pressure regulator, the air in it is compressed until it can force itself through the liquid with the vapor of which it is to be saturated.

*The Manometer* is intended to measure the amount of this compression or the internal pressure; it is made of ordinary

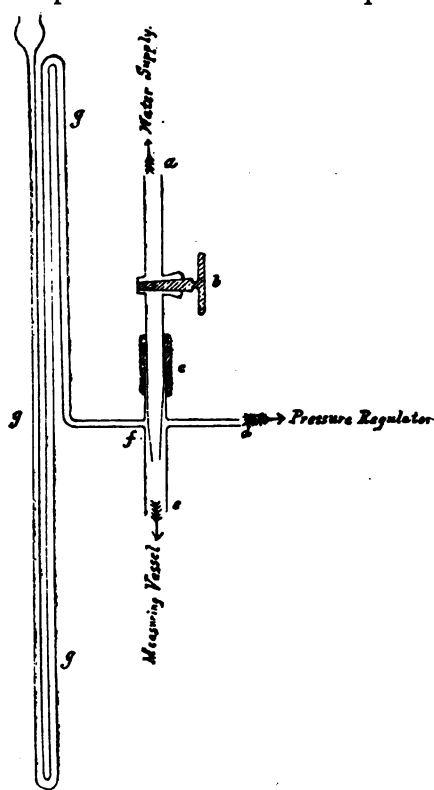


FIG. 1.

glass tubing bent into U shape, with the branches about two feet long. It may be put between the measuring vessel and the pressure-regulator, or between the drying tubes and the latter; I have found it most convenient, however, to melt it into the vertical branch of the T tube of the measuring vessel just opposite the horizontal branch, as shown in Fig. 1. The manometric liquid is water, and the differences of the heights of the liquid columns of the two branches, is read to a millimeter by means of a metric rule; the readings are then easily exact to a tenth mm. of mercury.

*The Drying Tubes* can, of course, be of various shapes and filled with various drying agents. Liquids, such as strong sulphuric acid, must be rejected, however, as they increase the internal pressure, and often cause an irregularity in the flow of the gas. I found U tubes to be the best shape, and grains of

pumice stone, soaked in concentrated sulphuric acid, the best drying agent; a length of at least sixty centimeters is to be taken, and the pumice must be changed often. When it becomes necessary, in work on acid solutions, to remove the carbon dioxide from the air, an additional tube filled with soda lime is taken. At the end of the last U tube, a mercury valve is attached to prevent the backward diffusion of the vapors; this is of the smallest size convenient, and the delivery-tube dipping into the mercury of capillary dimensions.

*Second Principal Part of Apparatus.* This is the absorption vessel, which may consist of a simple potash bulb according to Mohr. I found it better, however, to add two more bulbs, making five small and two large ones. As liquids which dissolve rubber somewhat were often introduced into the apparatus, and as it was necessary to let it stand sometime before weighing, the outlet and inlet tubes were provided with tiny ground glass stoppers. At first the bulbs were shut up in a copper case set in the thermostat; the case had holes in its sides, below the surface of the water, for the conduction and abduction of air, platinum capillaries and ground glass caps being employed to make the connections. This arrangement was not, however, found satisfactory, since one was never sure, air being such a bad conductor of heat, that the contents of the bulbs had the same temperature as that of the bath. Also, the platinum tubes proved to be very delicate, breaking readily if bent often, which was inevitable. It was accordingly found best to plunge the absorption vessel directly into the water of the bath, connection with the system of drying tubes being made with a bit of stout rubber tubing of small bore. When the vessel was removed from the water it was carefully wiped dry and set in the balance case, the atmosphere of which was kept dry by means of concentrated sulphuric acid.

*Third Principal Part of Apparatus.*—In order to analyze the mixture of vapors issuing from the absorption vessel two modifications of this part of the apparatus are required—one to be employed when the gaseous mixture contains a halogen compound of carbon, and the other when it contains an acid. In the first, the compound was decomposed by heated lime, and, in the sec-

ond, the acid was absorbed by a solution of potash or baryta. In the following lines a description of each is given:

(1) The outlet tube of the absorption apparatus is fitted by means of a good cork into one branch of a U tube of rather thick glass; this branch is bent at right angles at about the middle of its length, while the other branch is left straight. The latter branch is held clamped to a heavy and hence steady retort-stand set beside the thermostat, and is connected by means of a narrow lead tube to a tube of hard glass placed in the gutter of a combustion furnace. In the further end of the hard glass tube, a Maquenne absorption apparatus, containing a little dilute nitric acid, is inserted, the connection being made with a rubber stopper; this outlet of the absorption apparatus is in communication with a suction pump, and in the rubber tube making this connection a J tube is interposed, over the open end of which is slipped a piece of rubber tubing long enough to reach to the thermostat. When this tube is open, the interior of the apparatus, up to the liquid in the absorption vessel, is under atmospheric pressure; if it be pinched together a little so as to prevent enough air to feed the suction pump from entering, the pressure in the apparatus may be made less than that of the atmosphere; by this little device it is possible to regulate the pressure with great nicety.

(2) This analyzing apparatus consists simply of a potash bulb, according to Liebig, made of thick glass; one branch is flared out to receive the outlet tube of the absorption vessel, and the other is straight so as to glide up and down in a clamp of a retort stand.

The pieces of apparatus just mentioned will receive complementary description in the directions for performing experiments.

*Performance of an Experiment when the Mixture Contains an Organic Halogen or Sulphur Compound.*—The hard glass tube (about eighty cm. long) is filled with lime or sodium carbonate just as in a determination of halogens in organic analysis, joined to the lead tubing which establishes communication with the U tubes held in a clamp just above the surface of the water in the thermostat, and placed in the furnace. The gas is now lighted and the tube with its contents heated up to a red heat, while a

current of dried air is passed through it to remove all moisture.

The measuring vessel, the pressure-regulator, and the system of drying-tubes are joined air-tight together, and so set in the thermostat that as much room as possible is left for the absorption vessel.

The absorption vessel is filled with the liquid or solution under examination, a few bubbles of air drawn through so as to get the liquid beforehand in the right position, and carefully weighed. It is then connected with the U tube (of course, no air is now being passed through the analyzing tube), and after a couple of minutes of half submersion in the bath, it is attached to the system of drying tubes. It is now wholly submerged in the bath and air is made to pass through it as follows :

The stop-cock of the pressure-bottle is opened so that water may be run in slowly and, by compression of the air, gradually increase the internal pressure. As soon as bubbles of air commence to pass out of the absorption vessel, the stop-cock of the pressure-regulator is closed, and that of the measuring vessel opened. The water issues in drops or a fine stream in full sight of the operator, and its rapidity of flow can be very easily regulated. Experience has taught me that about a liter an hour was about the best rate; after a brief acquaintance with the apparatus, it is possible to judge very closely from the rate of the flow how long it will take for the measuring vessel to become filled. While the operation is proceeding, the height of the manometric column is read off at several different times; if the rate of flow is constant this does not vary by more than one or two mm. of water, or less than one-tenth mm. of mercury.

The barometer is also read off at the beginning and at the end of the experiment; in all my determinations, the difference of the two readings was less than one mm. of mercury.

A minute or so before the measuring vessel is full, the absorption bulbs are lifted out of the water enough to bring the end tubes about two inches above the surface, and there, together with the joining tube on one side and the cork and end of U tube on the other, are carefully dried with filter-paper. When the water in the measuring flask has reached the mark on the T tube (level of cork), the absorption vessel is detached from the dry-

ing tubes, and the little glass stopper fitted into its inlet tube. Immediately after this operation, the connection between the absorption vessel and the U tube is broken, and as soon as this is done a perforated cork, through which passes a narrow glass tube so bent at right angles that a long vertical branch is obtained is fitted into the U tube, its object being to prevent the escape by diffusion of any portion of vapor contained in the U tube. A current of air is now drawn through the tubes, slow at first to avoid causing too much vapor to pass over upon the heated lime all at once, as, if there be a deficit of air, the combustion is incomplete, and free carbon collects in the cooler portion of the tubes; in a well conducted experiment, the lime should remain perfectly white. Towards the end of the determination, a more rapid stream of air is drawn through the apparatus, so that one may be sure that all the halogen compound has been brought into contact in the decomposing agent. If any free carbon collects in the tube or if the dilute nitric acid in the Maquenne absorption bulb shows on the addition of silver nitrate the slightest trace of cloudiness, the determination ought to be rejected as untrustworthy.

The absorption vessel, as soon as possible after its removal from the water in the thermostat, should be closed with the second tiny stopper, wiped dry, and set in the balance case, where it takes on the temperature of the room. When this is thought to have taken place, it is weighed, and the loss of weight set down as the evaporated quantity of solution. When the furnace has cooled down, the lime tube is removed and its contents washed out with water and nitric acid into a flask, which is set over a flame and boiled until complete solution ensues, more nitric acid being added, if necessary. If more than a half gram of the halogen compound has evaporated, the solution is brought to a certain volume and an aliquot portion of it taken for analysis.

Most of the analyses were made by the gravimetric method of determination of halogens by precipitation with silver nitrate; some, also, were analyzed volumetrically, Volhard's method being employed.

*Performance of an Experiment when the Mixture contains an Acid.*—The absorption vessel is filled with the mixture being



investigated, and weighed as described above. It is then joined by means of a good cork to the analyzing apparatus, into which are run from a pipette ten cc. of a stock solution of potash or baryta; the pipette being provided with a straight calcium chloride tube filled with soda lime, all contamination from the carbonic acid of the breath is avoided. The alkaline liquor is of such strength that it is more than sufficient to neutralize the vaporized acid. The further end of the analyzing arrangement is closed with a U tube filled with soda lime so that the alkaline solution may be in contact with an atmosphere free from carbon dioxide.

The two pieces of apparatus thus filled and joined together are submerged in the water of the thermostat, the whole being held in place with a clamp embracing the upright tube of the analyzing contrivance and attached to a heavy retort stand. The other end of the absorption vessel is then placed in communication with the drying tubes, etc., by means of a short bit of stout rubber tubing.

The internal pressure is regulated and the air passed just as described in the preceding section, note being taken of the amount of internal pressure, the volume of the air and the barometric height. A slight correction has to be made to the barometric reading for the following reason: after the air passes the liquid contained in the absorption vessel and comes into the analyzing tube, it is under a pressure equal to that of the atmosphere plus that due to the weight of a column of liquid corresponding to the difference of level between the two surfaces of the alkaline solution; this, in my apparatus, was determined to be equal to one mm. of mercury, which was added to all barometric readings.

When the measured volume of air has passed through the apparatus, the stop-cock, through which water enters into the measuring vessel, is closed, the absorption and analyzing vessels are lifted nearly out of water, and after the joint between the absorption vessel and the system of drying tubes has been wiped dry, it is broken. Both the pieces of apparatus are wiped dry with bibulous paper, and agitated somewhat so that any acid vapors in the bulbs may be brought in contact with and absorbed by the alkaline liquor.

The pieces are then disconnected, the absorption vessel stoppered and set in the balance-case, while the contents of the analyzing vessel are poured into a beaker, rinsing being done with water free from carbon dioxide. Without delay, the excess of alkali is estimated by titration against deci-normal acid solution, and by a simple calculation, the quantity of evaporated acid is obtained.

#### 4. CALCULATION OF RESULTS.

In the calculations it is assumed that the laws of perfect or ideal gases may be applied to the mixtures of vapors; that is, the laws of Boyle, Gay Lussac, and Dalton. Where not too much vapor is present in the gaseous mixture the legitimacy of this assumption is unquestionable; and even though this condition be not fulfilled, the approximation to accuracy may be sufficient (see section 6).

*Calculation of Volume of Air Passed Through a Mixture.*—In order to force the air in the measuring vessel through the liquid in the absorption vessel, it is necessary that it be brought under a pressure equal to that of the atmosphere plus that required to vertically displace the liquid contained in the bulbs, the latter pressure varying with the density and amount of the mixture. The volume of the air under atmospheric pressure may be obtained then as follows:

Let  $P$  represent the pressure of the atmosphere. Let  $P'$  represent the pressure which forces the air through the liquid. Let  $V'$  represent the volume of air under the pressure  $P + P'$ . Let  $V$  represent the volume of air under the pressure  $P$ .

According to Boyle's law, and inasmuch as the temperature remains constant,

$$V = \frac{(P + P') V'}{P}$$

*Calculation of Composition of Mixture of Liquid Vaporized.*—As this calculation is simply one of quantitative analysis, it is not necessary to treat of its details.

*Calculation of Partial Volumes of Mixtures of Vapors.*—Let  $m$  represent the quantity of one component in the gaseous mixture. Let  $M$  represent its molecular mass. Let 22.32 represent the volume in liters of a gram-molecule of hydrogen at the tem-

perature  $0^\circ$  and under the pressure 760 mm. Let  $\alpha$  represent the coefficient of expansion. Let  $v_1$  represent the volume of vapor at the temperature of the determination  $t$  and under the atmospheric pressure  $p$ . We then have

$$v_1 = 22.32 \frac{m}{M} \times \frac{760(1 + \alpha t)}{p}.$$

*Calculations of Partial Pressures of Components of Vapor Mixture.*—Let  $v_1$  represent partial volume of one component. Let  $v_2$  represent partial volume of the other. Let  $v$  represent partial volume of air. Let  $p_1$  represent partial pressure of one component. Let  $p_2$  represent partial pressure of the other. Let  $p$  represent the atmospheric pressure.

In accordance with Dalton's law,

$$p_1 = p \frac{v_1}{(v + v_1 + v_2)}$$

and

$$p_2 = p \frac{v_2}{(v + v_1 + v_2)}$$

## 5. DISCUSSION OF SOURCES OF ERROR IN APPARATUS.

In order to make a just estimate of the degree of accuracy attainable by the above described apparatus, it is necessary to consider somewhat in detail the possible sources of error that may accompany a determination of the vapor-tension of a liquid made by it.

*Error in Measurement of Volume of Air Passed Through the Absorption Vessel.*—At the beginning of an experiment, both surfaces of the liquid under examination are under atmospheric pressure; by compression of the air in the reservoirs and drying tubes it is forced through the system of bulbs of the absorption apparatus. If, in all experiments, the same volume of liquid be taken, the amount displaced will be the same, and the internal pressure will be greater or less, according as the liquid employed is more or less dense. The internal pressure in some determinations varies slightly during their performance; the variation, however, never exceeds a millimeter or so of mercury. The use of a column of water to measure the internal pressure renders its determination very exact. The atmospheric pressure was found

to remain practically constant during an experiment, which seldom lasted more than an hour and a half. The error arising from the determination of the pressure to which the air in the interior of the apparatus is subjected, can accordingly be reckoned so slight as to be entirely negligible.

The mercury filled into the measuring vessel for the ballast, as well as the volume of water used to calibrate the same, can be measured to within a half cc., and as from 100 to 300 cc. of mercury and 1,000 to 3,000 cc. of water were taken, the error committed cannot be more than a thousandth of volume of air, and, in most cases, is probably less.

The air is, from the way it is forced from the measuring vessel, always measured when saturated with aqueous vapor. The drying tubes are always to be so filled with the drying reagents as to leave as little room as possible; I found, however, by special experiments, that the shape and size of the drying tubes exercise no appreciable influence upon the quantity of liquid carried off by the air; the only requisite seems to be that they dry the air thoroughly.

All the parts of the apparatus employed in measuring the volume of air being completely submerged in the water of the thermostat, there is no possibility of error arising from non-uniformity of temperature. The temperature of the water which expelled the air was, in most of my experiments, about  $20^{\circ}$  lower than that of the thermostat, but it entered the measuring vessel so slowly that it took on the temperature of the bath without disturbing, to any appreciable degree, the prevailing thermal conditions. That the water introduced took on rapidly the temperature of the bath was proven by the circumstance that, when, at the end of a determination, the flow of the water was stopped, and the level of the letter was flush with the gauge-mark, if the measuring vessel, which in this condition might be said to be a rude but still quite delicate thermometer, was allowed to stand undisturbed for some time, no expansion or, at most, but very slight expansion of the water occurred.

*Error from Change of Concentration of Mixture.*—A source of error is to be found in a possible change of the concentration caused by one or the other of the components of the mixture

being carried off by the air in such quantity that the composition of the residual mixture is not the same as at the beginning of an experiment; I think, however, that the error introduced in this manner is so slight as to be practically negligible, and for the following reasons:

1. The shape of the absorption vessel is such as to form five chambers almost entirely independent of one another as far as their contents are concerned. The stream of air becomes saturated in passing through the first two or three bulbs, and passes through the last two without changing, to an appreciable degree, the composition of the mixture contained in them. That saturation is complete after the air has been passed through the first three bulbs, I assured myself by special experiments; that is, I filled only the three first bulbs, and found, on passing a certain volume of air through them, that the evaporated quantity of liquid was the same as when the same volume of air under similar conditions was passed with all the bulbs filled with the liquid.

2. As from forty to eighty grams of solution were taken in a determination, and as the quantity evaporated rarely exceeded two grams, it is evident that, even if, towards the last of the experiment, the concentration of the first bulb had altered somewhat, the composition of the mixture in the fifth bulb would remain practically unchanged.

3. Most of the mixtures examined were made up of liquids possessing not greatly different vapor-tensions, so that the vapors of both liquids passed off in about the same proportions.

*Error in Analysis of Mixture of Vapors.*—The mixture of vapors on escaping from the absorption vessel passes into the U tube, and thence through the lead tube into the analyzing tube. In order that no vapor may condense in the end of the U tube flared out for the reception of the cork through which passes the outlet tube of the bulb apparatus, the latter tube is ground into the horizontal branch which is somewhat constricted for that purpose; the cork is employed to give solidity and stiffness to the juncture. It is believed that by this means all the vapor passes into the horizontal branch of the U tube where it is directly exposed to the action of the entering current of air.

Necessarily, the outer branch of the U tube has to project a little out of the water of the bath in order that the lead tube may pass over the side of the thermostat; hence, as the upper part and the lead tube are generally at lower temperature than the water of the bath, some condensation of the vapors occurs; the condensed vapor runs down the tube to collect at the bottom. In order to vaporize this liquid and cause it to pass over the glowing lime, it is necessary to pass a current of air through the tubes to complete the determination. In this operation, two sources of error may be encountered: First, when the connection between the absorption vessel and the U tube is broken, some of the vapor with which the tubes are filled may diffuse out and be lost; and second, the vapor may be carried along too rapidly with the air to permit of its complete decomposition by the heated lime. There seems to be no simple means of avoiding slight loss of vapor; still, by careful manipulation and rapid operation, the loss may be rendered insensible.

My mode of operation was as follows: Holding between the thumb and first finger of my right hand the little stopper of the absorption vessel, and between the thumb and the first finger of my left hand the cork and tube to be fitted into the horizontal branch of the U tube, I withdrew the cork, and at once inserted in the U tube the cork and tube. The time that the ends of the pieces of apparatus were open was less than two seconds, so that the loss must have been minimal.

A circumstance which aids in the prevention of loss by diffusion is, that the heated lime tube causes a slight draft towards it when the U tube is open. It is certainly legitimate to conclude that the error from this source is exceedingly slight.

In regard to the second source of error the greatest precautions must be taken to prevent its assuming disturbing proportions. As soon as the connection between the absorption vessel and the U tube has been secured, the pinch-cock on the end of the rubber tubing (see page 633) is closed a little so that air is drawn in a slow stream through the tubes at first, and faster afterwards (see page 634). The amount of error due to this source is best determined by special experiments in which a weighed quantity of a pure halogen compound is introduced

into the absorption vessel, a certain volume of air passed through it, all the usual precautions in determining a vapor-tension being observed, and a comparison made between the loss by vaporization and the amount of the compound calculated from the quantity of halogen found in the lime; naturally the loss should, in case no error of experimentation has occurred, be equal to the quantity of liquid corresponding to the halogen found by analysis. Two experiments were carried out, one with carbon tetrachloride, and the other with chloroform. The difference between the weights and the liquids before and after the passing of the air was for chloroform 1.9014 grams, and for carbon tetrachloride 2.0178 grams; the results of analysis gave the amount of chloroform to be 1.9022 grams and that of carbon tetrachloride 2.0167 grams. As is seen, the differences between the two sets of results are not more than those due to the errors of analysis, and it seems that the error due to the analysis of the mixture of the vapors is very slight.

When an acid is in the mixture whose vapor-tension is being determined, the error attendant upon the determination of the amount vaporized cannot be more than that incurred in a titration, since there is no chance for the acid to escape, so quickly and directly is it brought in contact with the absorbing alkaline liquor. In a special experiment, the loss of acid from the absorption vessel was 0.2908 grams, while a titration of the solution of baryta gave as the amount of acid 0.2896 grams.

While the errors of the experimental method here described seem to be slight, there is an error that may have been committed in the assumption which lies at the basis of our calculations; when the volume of a vaporized liquid is large in comparison with the total gaseous volume, it is very probable that the vapor cannot be likened even approximately to an ideal gas. This point will be discussed in the following section.

#### 6. COMPARISON OF THE VAPOR-TENSIONS OBTAINED BY THE METHOD HEREIN DESCRIBED AND THOSE OBTAINED BY OTHER METHODS.

Probably the best way to judge of the accuracy of the results

obtained in the determination of the vapor-tensions of liquids according to the method described in this paper is to compare them with the results obtained by other investigators working by other methods. Also a criterion of accuracy is to be found in the more or less close concordance of duplicate experiments. In the following table are given the necessary data of my experiments together with the results obtained by others. It was in some cases necessary to interpolate the results of others inasmuch as my results referred to a limited number of temperatures; the interpolations were made on a large scale, so as to avoid any slight inaccuracy. The original papers of Young and Regnault I am now unable to consult, and have to take their data as given in Landolt and Börnsteins "Physikalisch-Chemische Tabellen" or other reproductions.

TABLE II.<sup>1</sup>  
*Vapor Tensions of Pure Liquids.*

Name of liquid.	Temperature.	Loss in grams.	Volume of loss in cc.	Volume of air in cc.	Internal pressure in mm. Hg.	Barometer in mm. Hg.	Tension of vapor in mm. Hg.	Tension according to other observers.
Benzene.....	34.8°	1.3805	443.	1876	5	760	145.4	147.2 (Y)
Monochlorobenzene ..	34.8°	0.2291	5.1	1883	10	757	20.3	20.0 (Y)
Monobrombenzene ..	34.8°	0.1289	2.0	1888	10	757	8.0	8.0 (Y)
Toluene.....	34.8°	0.2451	67.6	1014	11	754	46.8	
" .....	34.8°	0.4672	128.9	1949	11	754	46.7	
Metaxylene (not especially purified) ..	34.8°	0.1080	25.8	1201	17	757	4.17	
Metaxylene (not especially purified) ..	34.8°	0.1085	25.9	1201	17	758	4.18	
Nitrobenzene.....	34.8°	0.0090	1.85	1210	23	757	1.16	
" .....	34.8°	0.0088	1.83	1207	21	757	1.15	
Carbon tetrachloride.	34.8°	3.3803	5.55	1913	20	758	169.4	172.6 (R)
" .....	27.8°	2.4031	3.96	1908	18	756	130.0	130.8 (R)
Chloroform .....	35.0°	3.0320	64.48	1033	25	755	290.1	301.1 (R)
Ethyl iodide .....	34.8°	4.2091	683.	1913	20	756	199.0	206.0 (R)
" .....	27.8°	2.9760	483.	1918	22	756	152.2	154.7 (R)
Carbon bisulphide...	20.0°	2.4541	777.4	1206	21	756	296.4	298.1 (R)
Methyl formate .....	20.0°	5.1090	195.8	1196	16	756	469.4	
Acetic acid .....	35.0°	0.2900	70.0	1960	20	760	26.3	26.5 (R&Y)

An inspection of the table shows a most excellent correspond-

<sup>1</sup> Bibliographical references to Table II: (Y)=Young; Chem. Soc. 55, 486, 1889. (R)=Regnault; Mémoires de l'Académie, 26, 239, 1862. (R & Y)=Ramsay & Young, Chem. Soc., 49, 790, 1886.



ence between my determinations of vapor-tensions and those of others, when the liquid is but slightly volatile, as in the case of the halogen substitution products of benzene. But when, at the temperature taken for a determination, the elastic force of the vapor exceeds one hundred mm. of mercury, the correspondence becomes less close; and it is at once seen from the data that the greater the volatility of a liquid, the greater the discrepancy. Let us take carbon tetrachloride and ethyl iodide for examples, since determinations of their vapor-tensions were carried out at two different temperatures. For carbon tetrachloride the difference between Regnault's results and mine is three and two-tenths mm. of mercury at  $34.8^{\circ}$  and eight-tenths mm. of mercury at  $27.8^{\circ}$ ; for ethyl iodide, the difference at  $34.8^{\circ}$  is seven and one-tenths mm. of mercury, and at  $27.8^{\circ}$  one and five-tenths mm. of mercury. Other examples point to the same result.

The cause of this want of concordance between my results and those made by other methods has been hinted at in the last paragraph of the discussion of the errors to which this method is subject. The assumption, made in the calculations, that the vaporous mixture may be treated as a mixture of ideal gases, cannot be maintained when the volume of the vaporized liquid forms more than a small fraction of the total volume of the gaseous mixture that leaves the absorption vessel. The vapor of ethyl iodide that was carried off by the air, occupied more than a fourth of the total volume, and the other volatile liquids also occupied relatively large volumes; the volumes of the vapors of the less volatile liquids, however, were but a small part of the volume of the air passed through the liquid. And, as has been shown, the less volatile liquids give results perfectly concordant with those obtained by others. Duplicate determinations of the vapor-tensions of some of the liquids, as toluene, nitrobenzene, etc., give almost identical results.

It would not be difficult to apply a correction taking into account the greater volatility of some of the liquids. This I have not, as yet, done, as in certain details I wish to alter the apparatus so as to obtain even more accurate results; thus the use of mercury as the liquid for expelling the air from the measuring

vessel would render the system of drying tubes unnecessary; also ground glass joints are undoubtedly preferable to rubber connections. Although it is my intention to study and modify the apparatus further, I do not want to seem to "reserve" this subject of investigation; on the contrary I would be most glad to see the apparatus tried and tested by others.

Although the results obtained by the employment of this method do not have in the case of the more volatile liquids the same degree of accuracy attainable by other methods, still they are suited to the requirements of an investigation of the vapor-tensions of mixtures of liquids, since both liquids, if their vapor-tensions be not too different, are affected alike by any weaknesses in the method, and the phenomenon observed permits of the drawing of theoretic conclusions. Yet I have been careful in the discussion of results to limit myself as much as possible to such as were of the same accuracy as results obtained by others; thus, my method can be counted upon to give results accurate to less than one mm. of mercury when the vapor-tension does not exceed 100 mm. of mercury, and to less than two mm. of mercury when the vapor-tension is less than 150 mm. of mercury; as can at once be seen by a comparison of the data due to Young (*loc. cit.*) and Regnault (*loc. cit.*) in the greater number of cases a closer correspondence than to within two mm. cannot be found. However, the conclusions which I draw from my experiments would still hold if the error in the determination were several times greater than that admitted above, inasmuch as it affects each liquid in the same way, so that, while it may affect the absolute accuracy, its relative effect is but slight.

#### 7. CHOICE AND PURIFICATION OF LIQUIDS.

As stated previously, the liquids employed in the course of this investigation were those recognized to be strictly normal; and of those only such were chosen as can be gotten in a state of great purity. The only associated liquid taken was acetic acid, whose degree of association as well as whose physical properties are to a certain extent known.

An associated liquid was investigated for the purpose of apply-

ing the regularities and "normalities" discovered in mixture of normal liquids to mixtures of a normal liquid with an associated liquid. Great pains were taken to purify the liquids in the highest possible degree, it being the testimony of all those who have occupied themselves with experimental work on the vapor-tensions of liquids that even very slight impurities have a remarkably disturbing effect upon the accuracy of results; this is especially the case in results obtained by the static method; in the method employed by me, the influence of a slight amount of impurity is not so marked; still, for all that, it has been thought best to employ such material as had been most thoroughly purified.

In order that the readers of this paper may judge for themselves the degree of purity of the liquids examined, a somewhat detailed account of the method of purification of each liquid is given together with a statement of certain characteristic physical properties of each. All of the liquids, it may be stated beforehand were bought as chemically pure from the dealers (Poulenc Frères, Paris, and Billault, Paris), and at least one pound—generally two or three pounds—subjected to the purifying operations.

*Benzene*.—Nearly three pounds of benzene—labelled chemically pure and free from thiophene—were treated a half dozen times with sulphuric acid to remove last traces of the sulphur compound. The liquid was then repeatedly fractionally crystallized until about a pound was obtained melting at  $5.3^{\circ}$ . This purified product when partially solidified showed, no matter what the proportion of liquid and solid was, the same melting point. The whole was then distilled over a few pieces of sodium, no variation from the boiling point  $80.1^{\circ}$  under a pressure of 756 mm. of mercury being observed. Its specific gravity at  $25^{\circ}$  referred to water at the same temperature was found to be 0.876611.

*Toluene*.—Of the quantity of toluene taken for purification (about two pounds) more than four-fifths distilled at  $109.8^{\circ}$  to  $110.1^{\circ}$ , an indication that the commercial article was nearly pure. After a couple of distillations over a little sodium, more than a pound was obtained boiling constantly at  $110.1^{\circ}$  under a pres-

sure of 758 mm. of mercury. Its density at 25° referred to water at 25.0° was ascertained to be 0.86288.

*Monochlorbenzene*.—A couple of pounds of monochlorbenzene were repeatedly distilled in fractions until a constant boiling product resulted. About three-quarters of a pound were obtained, boiling at 131.8° to 131.9° under a pressure of 757 mm. of mercury, and having a density at 25.0° (referred to water at same temperature) of 1.10362.

*Monobrombenzene*.—Nearly a pound of brombenzene was fractionally distilled until a distillate was obtained boiling between narrow limits. About 150 grams of the product, boiling at 154.3° to 154.5° under a pressure of 761 mm. of mercury were obtained. The density at 25° referred to water at 25.0° was 1.49852.

*Nitrobenzene*.—The commercial article was repeatedly crystallized until an almost colorless liquid was obtained, which when solidified, showed the same temperature during the remelting. It possessed a melting point of 3.6°, and its density was 1.20201,  $\left(\frac{25^\circ}{25^\circ}\right)$ .

*Chloroform*.—About two pounds of "chloroform anesthetique" of commerce were washed a dozen times with water, dried thoroughly by means of fused calcium chloride, and distilled. The larger distillate boiled at 60.8° to 61.0° under a pressure of 751 mm. of mercury, and finally nearly a pound was obtained boiling at 60.9° under a pressure of 755 mm. of mercury.

*Carbon Tetrachloride*.—Two pounds were washed with water, and thoroughly dried by means of concentrated sulphuric acid. The product was then rectified, and nearly a pound boiling throughout the operation at 76.6° under a pressure of 756 mm. of mercury taken for the preparation of the mixtures. The specific gravity of this product at 25.0° referred to water at the same temperature was 1.58828.

*Acetic Acid*.—Two pounds of glacial acetic acid were repeatedly fractionally crystallized until a portion melting at 16.7° was obtained. The bottle containing it as well as the mixtures made

from it were kept under an air-tight bell-jar by the side of very strong sulphuric acid.

#### 8. PREPARATION OF THE MIXTURES.

The mixtures were prepared by weighing out to a milligram on a balance turning with a tenth milligram the liquids in a flask; the corked flask was tared, the less volatile liquid poured in and weighed, and then the more volatile. As from forty to one hundred grams of the mixture were weighed out, the composition of the liquid was thus known to a ten-thousandth at least. The mixtures were preserved in bottles or flasks fitted with the finest corks, and kept in a dry, cool, dark closet. As, almost invariably, the necessary vapor-tensions of a liquid were made immediately after its preparation, no change of concentration occurred even with the most volatile liquids employed.

In the case of some of the mixtures of benzene and carbon tetrachloride, the residues of the investigated mixtures were united, and the amount of chlorine in the resulting mixture determined according to Carius' method.

The mixtures of benzene or toluene with acetic acid had their concentration controlled by an analysis. Five to ten cc. of the mixture were carefully weighed out in a glass-stoppered flask, water was added, which took practically all the acetic acid from the benzene, and then standardized baryta water run in to point of neutralization. In no case did the analysis give results sensibly different from those calculated from the direct weighings.

#### 9. EXPERIMENTAL RESULTS WITH MIXTURES OF NORMAL LIQUIDS.

In the following tables (III to X) are given those data of the experiments necessary for the calculation of the vapor-tensions. The superscriptions over each column of data render any preliminary mention here unnecessary. In some cases, the data have been represented graphically. (Figs. II. to IV.)

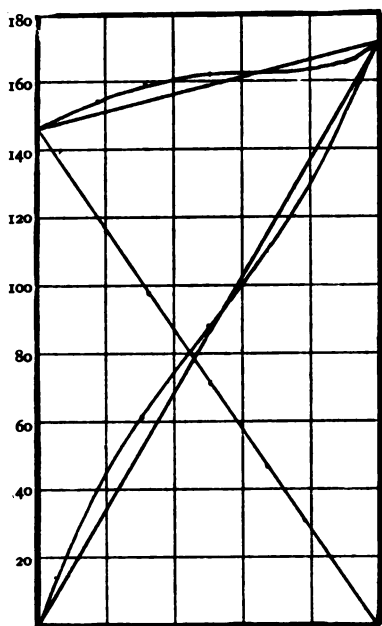


FIG. 2.

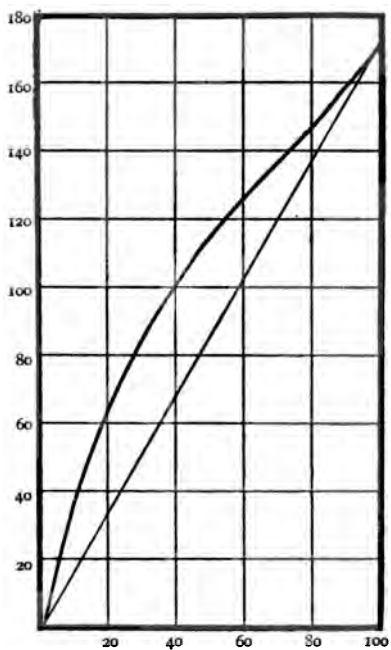


FIG. 4.

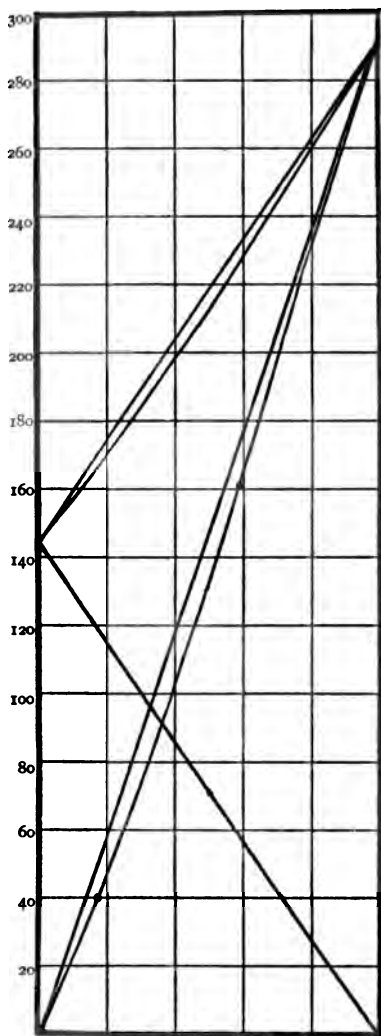


FIG. 3.

## EXPLANATION OF FIGURES.

Fig. 2.—Vapor-tensions, total and partial, of mixtures of benzene and carbon tetrachloride.

Abscissas = molecules of  $\text{CCl}_4$  in 100 molecules of mixture.

Ordinates = vapor-tensions in mm. of mercury.

Fig. 3.—Vapor-tensions, total and partial, of mixtures of benzene and carbon tetrachloride.

Abscissas = molecules of  $\text{CHCl}_3$  in 100 molecules of mixture.

Ordinates = vapor-tensions in mm. of mercury.

Fig. 4.—Vapor-tensions of mixtures of nitrobenzene and carbon tetrachloride.

Abscissas = molecules of  $\text{CCl}_4$  in 100 molecules of mixture.

Ordinates = vapor-tensions in mm. of mercury.

TABLE III.

*Vapor-Tensions of Mixtures of Benzene and Monochlorobenzene at 34.8°.*

*Vapor-Tension of Benzene at 34.8° is 145.4 mm. of Mercury.*

*Vapor-Tension of Chlorobenzene at 34.8° is 20.3 mm. of Mercury.*

Molecules $\text{C}_6\text{H}_5\text{Cl}$ in 100 mole- cules of liquid mixture.	Molecules $\text{C}_6\text{H}_5\text{Cl}$ in 100 mole- cules of gaseous mixture.	Grams $\text{C}_6\text{H}_5\text{Cl}$ in vapor.	Grams $\text{C}_6\text{H}_6$ in vapor.	Ten- sion of $\text{C}_6\text{H}_5\text{Cl}$ in mm.	Ten- sion of $\text{C}_6\text{H}_6$ in mm.	Vol- ume of air in mm.	Barom- eter in mm.	Internal pressure in mm.
15.18	1.33	0.0454	2.3075	1.7	124.6	3782	763	11
29.08	6.11	0.0857	0.9143	6.6	101.3	1900	757	17
65.06	19.37	0.1800	0.5202	12.3	51.3	2032	758	18
79.21	35.15	0.3572	0.4750	19.1	27.9	3787	756	12

TABLE IV.

*Vapor-Tensions of Mixtures of Toluene and Monochlorobenzene at 34.8°.*

*Vapor-Tension of Toluene at 34.8° is 46.8 mm. of Mercury.*

*Vapor-Tension of Chlorobenzene at 34.8° is 20.3 mm. of Mercury.*

Molecules $\text{C}_6\text{H}_5\text{Cl}$ in 100 mole- cules of liquid mixture.	Molecules $\text{C}_6\text{H}_5\text{Cl}$ in 100 mole- cules of gaseous mixture.	Grams $\text{C}_6\text{H}_5\text{Cl}$ in vapor.	Grams $\text{C}_6\text{H}_6$ in vapor.	Ten- sion of $\text{C}_6\text{H}_5\text{Cl}$ in mm.	Ten- sion of $\text{C}_6\text{H}_6$ in mm.	Vol- ume of air in cc.	Barom- eter in mm.	Internal pressure in mm.
18.96	9.84	0.0510	0.3821	4.3	38.2	1963	757	17
41.82	22.66	0.0985	0.2754	8.1	27.6	1973	760	21
76.71	67.79	0.2089	0.0821	17.5	8.2	1965	757	18

TABLE V.

*Vapor-Tensions of Mixtures of Benzene and Monobromobenzene at 34.8°.*

*Vapor-Tension of Benzene at 34.8° is 145.4 mm. of Mercury.*

*Vapor-Tension of Bromobenzene at 34.8° is 8.0 mm. of Mercury.*

Molecules $\text{C}_6\text{H}_5\text{Br}$ in 100 mole- cules of liquid mixture.	Molecules $\text{C}_6\text{H}_5\text{Br}$ in 100 mole- cules of gaseous mixture.	Grams $\text{C}_6\text{H}_5\text{Br}$ in vapor.	Grams $\text{C}_6\text{H}_6$ in vapor.	Ten- sion of $\text{C}_6\text{H}_5\text{Br}$ in mm.	Ten- sion of $\text{C}_6\text{H}_6$ in mm.	Vol- ume of air in cc.	Barom- eter in mm.	Internal pressure in mm.
30.33	24.30	0.0395	0.4975	2.6	103.1	1018	757	13

TABLE VI.

*Vapor-Tensions of Mixtures of Benzene and Chloroform at 34.8°.**Vapor-Tension of Benzene at 34.8° is 145.4 mm. of Mercury.**Vapor-Tension of Chloroform at 34.8° is 289.2 mm. of Mercury.*

Molecules CHCl <sub>3</sub> in 100 mole- cules of liquid mixture.	Molecules CHCl <sub>3</sub> in 100 mole- cules of gaseous mixture.	Grams CHCl <sub>3</sub> in vapor.	Grams C <sub>6</sub> H <sub>6</sub> in vapor.	Ten- sion of CHCl <sub>3</sub> in mm.	Ten- sion of C <sub>6</sub> H <sub>6</sub> in mm.	Vol- ume of air in cc.	Barom- eter in mm.	Internal pressure in mm.
16.97	24.30	0.3243	0.6607	39.6	123.5	1032	755	25
50.53	63.74	1.1513	0.4187	130.7	74.3	1030	756	25
59.47	73.25	1.4770	0.3531	162.2	59.2	1030	749	25

[TO BE CONTINUED.]

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF  
CHEMISTRY. No. 2.]

## THE ELECTROLYTIC DETERMINATION OF RUTHENIUM.

BY EDGAR F. SMITH AND HARRY B. HARRIS.

Received April 22, 1895.

FROM time to time efforts have been made in this laboratory to gather information upon the deportment of the metals of the platinum group toward the electric current. Palladium, platinum, and rhodium have been determined quantitatively, and also separated electrolytically from other metals of the group, *e. g.*, palladium from iridium. The purpose of this communication is to present data relating to the electrolysis of ruthenium salt solutions. The literature of electrolysis does not contain any information upon this point.

The salt upon which the experiments were made was the double chloride of potassium and ruthenium. It was prepared by fusing the finely divided metal with potassium nitrate and hydroxide. This fusion was made in a silver crucible. The aqueous extract was acidified with hydrochloric acid, and the solution was then evaporated to crystallization. Much potassium chloride separated at first, but finally the double salt appeared in minute red-colored needles.

The platinum dish in which the electrolytic decomposition was carried out was coated upon its inner surface with a layer of copper. In the first trials the solution of the double salt was mixed with three grams of sodium acetate, and acted upon by a current of  $N. D_{100} = 0.01-0.05$  ampere. The quantity of the ruthenium salt not being very abundant it was necessary to conduct the determinations with rather small amounts of material.



Thus, fifty cc. of the double chloride solution contained 0.0593 gram of ruthenium metal. The results of four trials were:

1 .....	0.0119 gram of ruthenium in five cc. of solution,
	equal to 0.0595 gram in fifty cc.
2 .....	0.0589 gram in fifty cc. of solution.
3 .....	0.0593 " " " "
4 .....	0.0590 " " " "

The metal deposit in each instance was dull black in color. A tendency to sponginess was also observed.

As other metals of the platinum group had been precipitated successfully from a phosphate solution (*Am. Chem. J.*, 13, 206) ruthenium was tried under similar conditions.

In the experiments that follow, fifty cc. of the salt solution contained 0.0407 gram of metal. Fifteen cc. of disodium phosphate (1.0358 sp. gr.) and one cc. of phosphoric acid were added to this solution. The current was of the same strength as that used in the first series of experiments. The metallic deposits weighed:

1 .....	0.0402 gram.
2 .....	0.0407 "
3 .....	0.0413 "

The ruthenium in each instance was bright and steel-like in appearance. It was also very adherent. There was not the slightest indication of sponginess. In the two series just given the deposit of metal was washed first with warm water, and subsequently with absolute alcohol. The period of precipitation continued through the night, although six hours were found to suffice for the complete deposition of the ruthenium.

In a third series of two trials, fifty cc. of the salt solution contained 0.0100 gram of ruthenium. The phosphate, phosphoric acid, and the current were the same as in the series immediately preceding. Results:

1 .....	0.0101 gram ruthenium.
2 .....	0.0100 " "

The deposits, as before, were bright and apparently crystalline.

Mention has already been made that palladium and platinum could be separated electrolytically from iridium (*Am. Chem. J.*, 16, 435) when present together with the latter in a phosphate solution. This was, however, not found possible with rhodium, although this metal was successfully deposited from a similar

solution. As ruthenium, from the results just given, allies itself with palladium, platinum, and rhodium, so far as its deposition from a phosphate solution was concerned, it seemed of interest to ascertain whether a separation of it from iridium could be effected.

*Separation of Ruthenium from Iridium.*—Here again a solution of ruthenium was used in fifty cc. of which there was 0.0100 gram of ruthenium. To this were added ten cc. of an iridium solution (equal to one-tenth gram of iridium), ten cc. of disodium phosphate, 1.0358 sp. gr., and three cc. of phosphoric acid. The current was  $N. D_{100} = 0.01$  ampere. It acted through the night. The deposit of ruthenium in each of the three experiments was bright, metallic, and perfectly adherent. It was washed and dried as in the determinations described in the preceding lines. Results:

1.....	0.0104	gram of ruthenium.
2.....	0.0096	" " "
3.....	0.0100	" " "

Additional experiments on the separation of the two metals were made with similar results.

It would be of interest and value to study the conduct of ruthenium in alkaline solutions. Wöhler<sup>1</sup> observed that the metal could be quickly brought into solution when the current acted upon it in the presence of an alkali. It is altogether probable that, under such conditions, its separation from the other metals of the group could be quite readily brought about, but lack of material will, at least for the present, prevent any such investigation.

UNIVERSITY OF PENNSYLVANIA.

---

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF  
CHEMISTRY. No. 3.]

## THE ACTION OF PHOSPHORUS PENTACHLORIDE UPON THE DIOXIDES OF ZIRCONIUM AND THORIUM.

BY EDGAR F. SMITH AND HARRY B. HARRIS.

Received May 31, 1895.

SOME years ago Weber (*Jahr. 1859*, 77) studied the action of phosphorus pentachloride upon inorganic oxides, such as those of silicon, titanium, and tin, and demonstrated that the

<sup>1</sup> *Ann. Chem. (Liebig)*, 146, 375.

products of the reaction were the corresponding metallic chlorides, together with phosphorus oxychloride. Tüttschew (*Jahr. 1867*, 205), working upon titanium dioxide with a modified method, obtained a double chloride corresponding to the formula  $\text{TiCl}_2 \cdot \text{PCl}_5$ .

It seemed to us of some interest to extend the study to the oxides of zirconium and thorium, thus completing the reaction with the more metallic bodies of Group IV of the periodic system. The procedure adopted by us consisted in introducing ignited and pure zirconium dioxide with its equivalent of phosphorus pentachloride into hard glass tubes, which were sealed after the air had been exhausted from them. The reaction appeared not to occur at  $150^\circ \text{C}$ ., but after heating to  $190^\circ \text{C}$ ., for a period of eight hours, a complete change was observed. A crystalline mass was noticeable and drops of phosphorus oxychloride were scattered through the tubes. These were opened at both ends and quickly connected with a chlorine generator, and distillation carried out by careful heating in an air-bath. Phosphorus oxychloride and some pentachloride were expelled. At  $190^\circ \text{C}$ ., crystals made their appearance in the cooler part of the tube, projecting beyond the air-bath. These were transparent and almost half an inch in length. That portion of the tube in which they had collected was severed, tightly closed, and weighed. It was then introduced into water. A hissing sound was quite distinct. Zirconium hydrate soon separated. After standing a while this was dissolved in dilute nitric acid, and reprecipitated with ammonia. Later it was found that to let the weighed chloride slowly absorb moisture from the air and then bring it into water insured better results. The percentage of zirconium found equaled 37.52 per cent., while the chlorine was 61.62 per cent. The theoretical requirements for the tetrachloride are 38.79 per cent. of zirconium and 61.21 per cent. of chlorine. Our zirconium result is low, yet the figures from three or four analyses concord so closely that there can be no question as to the correct nature of our product. A compound of zirconium chloride with either phosphorus pentachloride or oxychloride would require decidedly less zirconium and more chlorine. Hence, we can safely conclude that with our conditions

of experiment phosphorus pentachloride changes zirconium dioxide to the corresponding chloride. Thorium dioxide was subjected to a similar treatment. The temperature, however, at which the reaction seemed to proceed almost to completion was about  $240^{\circ}\text{C}$ . Exactly the same course was pursued in subsequently eliminating the excessive phosphorus compounds. The product analyzed showed the presence of a little phosphorus, not enough to establish the existence of a double chloride, therefore its quantity was deducted from the quantity of material used in the analysis. The thorium found equaled 62.23 per cent. and the chlorine 38.37 per cent., while the theoretical requirements for thorium tetrachloride are 62.23 per cent. thorium and 37.77 per cent. chlorine.

Our experiments supplement the investigations of Weber and justify the general inference that the dioxides of all the metallic members of Group IV are changed to tetrachlorides when heated under pressure with phosphorus pentachloride.

UNIVERSITY OF PENNSYLVANIA.

---

### NEW BOOKS.

A TEXT-BOOK OF CHEMISTRY INTENDED FOR THE USE OF PHARMACEUTICAL AND MEDICAL STUDENTS. BY SAMUEL P. SADTLER AND HENRY TRIMBLE. Octavo, pp 950. Philadelphia: J. B. Lippincott & Co., 1895.

The title on the cover is "Pharmaceutical and Medical Chemistry," from which it is to be regretted that the authors did not omit the word "Medical," as its use compels a remonstrance against the view which they apparently entertain, that the needs of the medical student in the department of chemistry do not extend beyond the study of the properties of drugs and the methods of chemical manufacture. Physiological, hygienic and toxicological chemistry are almost utterly ignored. A mere outline of the chemistry of urea is compressed into less than a page, while more than two pages are devoted to alizarin. Serum albumen is dismissed in four lines, without a word about the testing of urine for albumen. The discussion of the degrees of purity of natural waters is barely hinted at in a few lines, without any reference to the methods of examination of water, even

in the part devoted to analytical chemistry. The space allowed to the toxicological chemistry of arsenic is only three-quarters of a page, while the metallurgy of iron occupies four and three-quarter pages. To designate such a work as a "Medical Chemistry" is, to put it mildly, a misnomer.

Viewed, however, as a text-book for the use of the student of technical chemistry or the manufacturing pharmacist, the work is, in most respects, well arranged and, in the main, up to the times, although in some points somewhat too conservative. Such terms as acid potassium sulphate, copper sulphate, calcium phosphate, sodium sulphate, acid calcium phosphate, either have the ring of antiquity or lack precision. The orthography endorsed by the A. A. A. Sc. has not been adopted.

The work is divided into five parts. Part I contains, in 90 pp., a brief outline of elementary physics, which is rather popular and general than chemical or medical. The laws of Dulong and Petit and of Raoult are not mentioned, absorption spectra are merely referred to, and the description of the errors of refraction of the eye is not only fragmentary but misleading.

Parts II and III (182 and 243 pp.) treat of mineral chemistry. The elements are classified into "non-metals" and "metals," a division which widely separates nitrogen and phosphorus from their close relations to arsenic and antimony. Methane, ethane, acetylene, and the oxides and sulphides of carbon are treated of as universal substances in Part II. Descriptions of the methods of preparation of the elements and their compounds, and statistics of industrial production are detailed and illustrated by numerous familiar cuts of furnaces and other forms of manufacturing plants. Pharmaceutical references are in accordance with the last revision of the U. S. Ph.

Part IV (280 pp.), devoted to organic chemistry, is admirably written. The arrangement is logical and scientific, and the matter is abreast of the advances in this most important division of chemistry, and as full as is desirable or possible in a work of this size. But in this division, also, it is to be regretted that the space occupied by pictures and details of manufacturing apparatus and processes was not devoted to medical chemistry.

Part V (94 pp.) contains the analytical portion. The reac-

tions of bases and acids are given with conveniently arranged tabular schemes of qualitative analysis. There are also a few examples of quantitative methods, and descriptions of the more important processes of drug assay. The work concludes with an appendix containing useful tables. R. A. WITTHAUS.

JOHN DALTON AND THE RISE OF MODERN CHEMISTRY. BY SIR HENRY E. ROSCOE. New York and London. Macmillan & Co., 66 Fifth Avenue, New York City. Price, \$1.25. pp. 216; 12 mo. Portrait and facsimile. The Century Science Series.

This is an unusually satisfactory book; it is a pleasure to read the biography of one eminent man written by another distinguished in the same branch of knowledge, who appreciates and sympathizes with his subject and his subject's labors.

Materials for a history of John Dalton and his contributions to chemistry were not lacking. W. C. Henry's "Memoirs" (1854), R. A. Smith's "Memoir and History of the Atomic Theory" (1856), Charles Clay's "Reminiscences" (1884), and Lonsdale's "Worthies of Cumberland" (1874), supply the necessary details of the uneventful, quiet life of the Manchester schoolmaster, and accounts of his momentous researches in chemical philosophy. Besides these sources of information, Sir Henry could refer to his own lecture delivered in the Town Hall, Manchester, in 1874. In this volume we find a summary of Dalton's parentage, school days, and teachers, his experience as a school teacher when only twelve years of age, his first attempts at scientific investigation (meteorological), his connection with the Manchester College, and his pains-taking researches on the relative weights of ultimate particles. The text is pleasantly anecdotal, clearly describing Dalton's personality. The volume is illustrated with a portrait of Dalton, facsimiles of letter and leaflet containing the atomic symbols. One remark of Sir Henry's greatly surprises us; speaking of decimal fractions he says they are "a snare and a stumbling-block even to some great men of the present day." Can it be that calculations in  $\mathcal{L}$ ,  $s$ , and  $d$ . are so deeply impressed on the British mind that they prevent comprehension of decimals familiar to every American school-boy? The book contains an excellent index.

H. CARRINGTON BOLTON.





*Arthur E. Moore*



---

## DR. GIDEON E. MOORE.

Received May 31, 1895.

THE death of Dr. Moore happened on Saturday, April 13, 1895. On the following day the death of Prof. James D. Dana was announced. The occurrence so closely together of these sad events was a striking one, for it was under the guidance of Prof. Dana that Dr. Moore entered upon a field of study which he cultivated with so much ardor that his reputation for deep scientific work was increased; and we may well believe that, had not the accidents of fate and fortune turned Dr. Moore's steps from academic halls he, also, would have left the impress of his good and strong personality upon the mind and life of many a youthful student of science.

Gideon Emmet Moore, son of George H. and E. L. Moore, was born in New York City, August 21, 1842. His maternal grandfather, after whom he was named, was Dr. Gideon Humphrey, one of the leading physicians of Philadelphia in the beginning of this century, who distinguished himself as a surgeon in the war of 1812, and took part with remarkable adventures in the filibustering expeditions of the period. His father, whose family belonged in Maine, early went to California, in fact was one of the first settlers of San Francisco, as he was there eleven years before the Argonauts of '49. He embarked in the business of shipping and warehousing, and his firm was the foremost one of the time.

Young Gideon Moore's early days were spent, some in New York and some in Burlington, N. J., and, before entering Yale College, at Dr. Bartlett's Academy in Poughkeepsie. In his boyhood he was passionately fond of music and an accomplished performer on the violin. His class at Yale was '61. Prof. S. W. Johnson has kindly sent me the following tribute to his pupil:

"Our friend, Gideon E. Moore, entered the Yale Scientific School in the Autumn of 1859, graduated as Bachelor of Philosophy in the Summer of 1861, and remained as a postgraduate student until the Spring of 1862.

"During the first year of his attendance I knew him slightly, but from September 1860 until he finished his studies I had immediate charge of the Laboratory of Analytical Chemistry and was constantly familiar with his progress in chemical study. I was from the outset attracted by the gentle and courteous manners of the somewhat delicate appearing youth whose invariable cheerfulness, promptitude, and steady attention to work, no less than the ease with which he performed and exceeded the tasks assigned him, made the duty of his teacher a pleasure and a privilege.

"Having gone through an extended course of inorganic analysis with unusual rapidity and success he was well prepared to take up organic chemistry, and the proposal was made to him (I think in Sept. 1861) to undertake an investigation of Bayberry Wax.

"This research was foreseen to require a long time and to involve much tedious labor, but he entered upon it without hesitation, pursued it steadily for four months, and evidently enjoyed it heartily to the end.

"The results are embodied in his paper—'On the Chemical Constitution of the Wax of the *Myrica Cerifera*'—which appeared in the American Journal of Science, May, 1862. This short paper, of seven pages, presents a concise history of the chemical work previously done on the bayberry wax and established its nature as a mixture of about one-fifth part of tripalmitin and four-fifths nearly of palmitic acid with a little laurin or lauric acid. It illustrates the thoroughness which characterized his work and which made him so immediately successful when, soon after completing his studies at New Haven he engaged in the practice of analytical chemistry at San Francisco, and later when he became assayer to the Gould and Currie mine at Virginia City.

"As I write these lines there stands near by a series of twenty little bottles containing specimens of the fruit, foliage and wax of the bayberry and the preparations obtained during the research in question illustrating the method followed and showing the results arrived at. This instructive collection has done duty regularly for thirty-two years in my lectures and recalls vividly to my remembrance the busy days when our friend was diligently disciplining to extraordinary skill the hand that but a few hours ago suddenly forgot its cunning."

Yours very truly,

S. W. JOHNSON.

Dr. Moore's life in the West was hard enough to daunt the most courageous but he viewed it as a necessary step in his

progress. The rough life of the mining camp and the hardships of that primitive era had no terrors for him. The very task itself of keeping a foothold in such a community only spurred him to accomplish what he had set out to perform, just as in his college and professional career to suggest that a matter was difficult, was sufficient to fire his ambition to attack it and his confidence that he would overcome it.

After four years spent in this field, enjoying in the highest degree the confidence of the owners of the millions which passed through his hands, he resigned to embrace with enthusiasm the opportunity to secure what he had so long coveted—a thorough course at the German universities.

In 1867 he sailed for Europe and studied one year at Wiesbaden under Fresenius. He next went to Heidelberg and under Bunsen, Kirchhoff, Helmholtz, Blum, Vonderden, and Kopp he passed some of the happiest days of his life and was graduated *summa cum laude*. At Leipzig he studied under Kolbe one semester, and at Berlin in the laboratory of Wichelhaus.

In September, 1871, he married in Buda Pest, Marie Louise Von Hildebrandt, the daughter of Field Marshal Von Hildebrandt, of the Austrian army, and in the following month returned to America.

In 1872 he became chemist to the Passaic Zinc Co., and continued in that capacity to the close of his life. The remainder of his time was devoted to study and private practice, a field in which he rose to eminence and left a record marked with many triumphs.

Depth, care, thoroughness, and method characterized his work. His intellectual endowment was generous, his mental faculties keen, his memory good, his power of concentration wonderful. He possessed a logical and well-balanced mind not easily led to hasty conclusions. The virtue of strict, unwavering conscientiousness and fidelity to truth was a shining one in Dr. Moore, and his professional honor was not a mantle to be put on and off or to be distinguished from his personal honor. All his early training as well as the promptings of his heart fortified him in the practice of making diligent search for the truth, and having found it, of fighting bravely for his convictions.

He at one time wrote much and all of it was valuable; in the early days making many contributions to mineral chemistry; Brushite, Cryptocallite and Hetaerolite being additions made by him to the list of new species. Of late years his most laborious work, that on the "Chemistry of American Tobaccos," was written for the Tenth Census. He was editor of Vol. II of this JOURNAL, and in Vol. I appeared his report on the Progress of Analytical Chemistry for 1879—a model for all of its kind. He had taken out many patents in metallurgical and fuel-gas processes.

Subjoined is a list of his published papers:

1862. On the Chemical Constitution of the Wax of the *Myrica Cerifera*. American Journal of Science, [2], 33, 313.

1865. On Brushite, a new mineral species. American Journal of Science, [2], 39, 43.

1866. Analysis of the Water of Borax Lake, Cal. American Journal of Science, [2], 41, 255.

1870. On the occurrence of Amorphous Mercuric Sulphide (Metacinnabarite) in Nature. J. prakt. Chem., [2], 2, 319. American Journal of Science [3] 3, 36.

1871. On the Electrolysis of the Substituted Derivatives of Acetic Acid. Ber. d. chem. Ges., 4.

1875. On Chalcopyhanite, a new mineral species. American Chemist, July, 1875.

1877. On Hetaerolite, a new mineral species. American Journal of Science, [3] 14, 423.

1878. Report on the Strong System of Water-gas Manufacture. Engineering and Mining Journal, January, 1878.

1879. Report on the Progress of Analytical Chemistry, from April to September. J. Am. Chem. Soc., 1.

1883. Report on the Chemistry of American Tobaccos. Special Report of the United States Census, On the Culture and Curing of Tobacco. Chap. 22.

1885. Report on the Granger Water Gas. A. O. Granger & Co., Philadelphia.

1885. Kallait, pseudomorph of Apatite from California. In collaboration with V. von Zepharovich. Ztschr. für Krystallographie, Leipzig.

Dr. Moore's manners were gentle and courteous in the extreme. He used to tell with much appreciation how, when he was working in Bunsen's laboratory, he would always have to keep his eyes averted from Bunsen, who would immediately spring to his side were he to show the slightest sign of effort over the task or

the need of anything. And listening to him telling this you could not help thinking how marked was the same kindliness in himself. How grateful is association with such men. What a privilege to have daily converse with one whose soul delights in those little amenities which the throng overlook. What a pleasure in the cheery face. What a lesson we learn from the lips that may be quivering with pain, but open only to express solicitude for our welfare and to smile that they may hide their own story.

An acquisition that was of great value to our friend was his retentive memory. Everything that he had once mastered, whether in science or in other branches of knowledge, could be recalled to mind at will and with an accuracy and fidelity to detail that made us marvel. I remember on one occasion when in a leisure hour we were discussing the poets, and Coleridge became the subject of our remarks, he recited without hesitation the lines in *Kubla Khan*:

“But oh that deep romantic chasm which slanted  
Down the green hill atwart a cedarn cover!  
A savage place! as holy and enchanted  
As e'er beneath a waning moon was haunted  
By woman wailing for her demon lover!”

I said “You have been reading Coleridge lately?” “No,” said he, “I don't suppose that I have read these lines in over twenty years, but I remembered them for I always admired their sonorousness and picturesque effect.”

He was a poet himself of no mean order. His nature was essentially grave, retired and full of self-repression, yet it had that expanding joyousness which goes in search of the delights that we may draw from elevated themes and roseate imagery. He had translated much from Goethe, and more recently Hamerling, in lines which show alike his skill as a linguist and his art as a poet.

His end came suddenly, for he was stricken without warning, and he laid down his work to go and face the terrors of pneumonia. He did face them, and unflinchingly, and he calmly awaited the end, that he saw must come, with the fortitude of the Christian faith that he was glad to acknowledge.

CHAS. F. MCKENNA.

I spent last Saturday with Prof. T. E. Thorpe in his steam launch on the Thames at Kingston with a party of friends. He asked me then about Dr. Moore's death and spoke of him very warmly. They were students together in Germany and the friendship then formed was cemented by meetings during Thorpe's visit to America afterwards. He detailed at length, incidents of Dr. Moore's student and family life illustrating his lovable character.

Proof of Mr. McKenna's notice came to me in London, and I have ventured to add this note to show that his and Professor Johnson's words find an echo abroad.

EDWARD HART.

London, June 22, 1895.

---

### LOTHAR VON MEYER.

BY the sudden death of Lothar von Meyer, which occurred at Tübingen, on April 11th, chemical science has lost one of its foremost exponents.

It was vacation time in Tübingen, and Professor Meyer had returned from a walk and was engaged in his favorite outdoor pastime of trimming vines in his garden when he suddenly began to feel unwell and hastened to his study. He called for help and his wife and son went to his aid. Reaching a sofa with their support he remarked, "I have received a stroke," and then was able to say no more. This was at about 5 in the afternoon, and at 11 he died, without further struggle, his face retaining the calm and noble expression not to be forgotten by his many friends.

Julius Lothar Meyer was born August 19th, 1830, at Varel in the Grand Duchy of Oldenburg, the son of a well-known physician, Dr. August Meyer. He completed his gymnasium course in Oldenburg and began the study of medicine in Zürich in the Spring of 1851. There he spent four semesters, followed by two semesters at Würzburg, where he received the degree of Doctor of Medicine, in the Spring of 1854, for a thesis on the question of the condition of gaseous combinations in the blood. In the investigation of this problem Meyer's attention was attracted to the recent work of Bunsen on gas measurements, and accordingly we find him next in Heidelberg, where he re-

mained five semesters, at a time and in a company since famous in the history of chemistry. He took up again the question of the gases held by the blood, and in a long investigation, published in 1857, he showed for the first time the real nature of the oxygen absorption. Magnus had shown at an earlier date that the oxygen absorbed by blood did not follow the Dalton-Henry law, but he attempted no explanation for this fact. It remained for Meyer to determine the quantity of oxygen, carbon dioxide, and nitrogen absorbed under different conditions, and to show that the absorption of the first must depend on chemical combination. This investigation attracted immediate attention.

Meyer's tastes now led him away from medicine and in the direction of pure chemistry, and especially toward physical chemistry. Leaving Bunsen, he went to the old university of Königsberg, attracted by the courses of lectures given by Franz Neumann on the subject of mathematical physics. He remained with Neumann three semesters. In the Spring of 1858 Meyer went to Breslau, where he was given the degree of Doctor of Philosophy for a dissertation on the absorption of carbon monoxide by the blood. In this dissertation it was shown, for the first time, that CO displaces O, volume for volume. The author soon afterwards became a *Privatdocent* for physics and chemistry, and, in 1859, was given the position of Director of the Chemical Laboratory of the Physiological Institute. Here he remained until 1866. In this interval he published a number of valuable papers, and the first edition of his famous work, "Die modernen Theorien der Chemie."

In 1866 he was called to the Forestry Academy of Eberswalde, in 1868 to the Polytechnicum of Karlsruhe, and in 1876 to the University of Tübingen, where he had just completed his nineteenth year of labor at the time of his death.

Lothar Meyer was the author of numerous valuable scientific papers, most of which appeared in *Liebig's Annalen* and in the *Berichte*. They handle mainly questions from the field of physical chemistry. In some of his earlier papers Meyer began the study of the relations existing between the atomic weights and physical and chemical properties of the elements. Their relations were soon formulated in his Periodic System of the Elements.

That Mendelejeff arrived independently at almost the same conclusions does not, in any measure, detract from the originality or value of Meyer's work. It is this work which has made his name best known among scientific men, but without it his purely experimental investigations would be sufficient to give him a high position among the great chemists of the time.

In recognition of his services to science, Meyer received the Davy medal of the Royal Society in 1882, was made a Foreign Honorary Member of the London Chemical Society, in 1883, Corresponding Member of the Prussian Academy of Sciences, in 1888, and in 1891 a Corresponding Member of the Russian Academy. In 1892 he was given a title of nobility by decree of the Württemberg crown.

He was the author of the following works: "Die modernen Theorien der Chemie," first edition 1864, fifth edition 1884, a sixth edition the author had in preparation; "Die Atomgewichte der Elemente" (with Karl Seubert), 1883; "Grundzüge der theoretischen Chemie," first edition 1890, second edition 1893. The first and last of these books are well known in English translations.

It is not necessary, in this place, to speak of the high scientific value of Meyer's work, as that is a subject on which the literature itself speaks most plainly. He possessed great manual dexterity, and in glass-blowing and the construction of apparatus he had unusual skill. His style, as a lecturer, was simple and exceedingly clear, and in his everyday intercourse with students he displayed a kindliness of disposition and patience in explanation not often found with men whose time is as closely occupied as was his. Few investigators are willing to give from their private work the time which he freely gave to interested students.

Among his colleagues Meyer was cordially respected and beloved. Last summer he was appointed Rector of the University for the present year, and by other distinctions, as well, his popularity was shown. All who knew him mourn his loss as a man; chemists alone are able to recognize the loss to science.

J. H. LONG.

---



# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

---

### THE CHEMICAL HISTORY OF A CASE OF COMBINED ANTIMONIAL AND ARSENICAL POISONING.<sup>1</sup>

BY CHARLES A. DOREMUS, M.D., PH.D.

Received May 17, 1895.

THE coffin plate disclosed on opening the outer box of rough wood, bore the inscription, "Gustave H. M. J. Baum, died March 30th, 1892. Aged 26 years, 3 months, and 4 days." It was untarnished and affixed to a black cloth-covered casket. The condition, not only of the outer and that of the inner case, but also that of the lining of the latter and of the clothes about the body excluded the possibility of there having been any infiltration of liquid from the grave and rendered the examination of any soil from the cemetery superfluous.

The emaciated body of a medium sized man was identified by the physician who had attended him in life and verified his death and by the undertaker and his assistant who had prepared the body for burial.

Though three months had elapsed since the interment, it was possible on July 6th, 1892, to recognize the features, also an abrasion on the right shin. There was some mould about the face and body, the latter being disclosed when the clothing was removed. The features of the corpse bore a marked resemblance to a photograph of a man named Ludwig Brandt.

Both Baum and Brandt had been quondam acquaintances of a Dr. Henry Meyer. Insurance had been secured on the life of

<sup>1</sup> Read at the May Meeting of the New York Section.

Baum in four companies, amounting in all to \$8,500. Brandt had personated Baum in making application for these policies, had come to New York in company with Dr. Meyer, a woman posing sometimes as Mrs. Meyer, at other times as Mrs. Baum, and one Mueller.

After the death of Brandt the woman applied to the different insurance companies for the sums due, representing herself as his widow. Several of the companies paid in full, a total of \$4,000.

Accompanied by Dr. Meyer she visited the offices of the Mutual Life Insurance Co., of New York. The interview aroused suspicions which were subsequently increased by the sudden disappearance from New York of the parties, their effects having been sold and no word being left of their destination.

At the instigation of Mr. Daniel Gillette, of the Mutual Life Insurance Company, detectives were sent in search of the parties with the view of unearthing any crime that might have been committed. Mr. H. G. Julian, acting in this capacity, had been able to secure a description of the supposed Baum, and found the body to agree not with him but with a photograph and description of Brandt.

Dr. L. W. Schultze, one of the coroners of the city, deemed this initial evidence of sufficient weight to order an autopsy and conducted it with his medical assistants. Dr. S. P. Minden, who identified the body, had attended the man for three weeks before his death, and gave a death certificate ascribing the demise to chronic dysentery. He had not noticed any unusual circumstances during this attendance. Had not Dr. Meyer borne an unenviable reputation, it is probable that no further notice would have been taken of the case; but because of his career extra caution was taken at the autopsy to determine, if possible, if the pathological condition agreed with the diagnosis of the physician.

The surface of the body was carefully scrutinized. There were no marks of hypodermic injections, however, nor any evidence of embalming by arterial or other injections. The undertaker declared that no attempt was made to embalm the body and that no embalming fluid was used upon it or injected into

it. Three channels for the introduction of poison; *viz.*, imbibition from the soil, the use of embalming liquids, and the use of hypodermics were thus eliminated. Coroner's physician, Dr. O'Hare, and Prof. D. Hunter McAlpin, who at a subsequent time examined the viscera with Dr. O'Hare, could find no gross or microscopic pathological evidence of importance, so that full light as to the cause of death was not obtainable from the autopsy. At the autopsy Dr. S. P. Minden related the symptoms he noticed during his attendance on the patient. They did not develop any theory of death other than dysentery, but left the case still obscure. Later he kindly furnished copies of the prescriptions he had written. At the trial, testimony was given to show that some of these prescriptions had been filled but there was no evidence that the medicines had been administered. However, since remedies such as morphine, opium, copper arsenite, and bismuth subnitrate had been prescribed, it became necessary to consider them in any scheme of chemical analysis. The advisability of a chemical analysis was discussed and decided on as necessary to fully determine the cause of death. There was every probability that great skill had been used in the administration of any toxic agent or that some unusual poison had been employed.

Though due care was exercised at the autopsy to detect the odor of any volatile poison none was perceptible and there were no circumstances that in any way directed attention to that class of poisons. The analysis proper, therefore, was begun with the treatment of portions of the viscera for the alkaloids. For this purpose the stomach and its contents, one half of the intestine and its contents, and one-half of the liver, and some fluid which had exuded from it into the abdominal cavity at the time of the autopsy, were treated.

Freshly rectified alcohol was placed on each separate part, 500, 600, and 800 cc. being used respectively. The organs were comminuted and the alcohol acidulated with tartaric acid. The jars remained in an ice chest until a thorough maceration was effected. The alcohol and washings with alcohol was filtered from the tissue and the undissolved substances, which latter were utilized for the detection of inorganic poisons, as were also such other

residues from the extraction as could be utilized for this purpose.

The necessity for doing this is not generally recognized. Some of the salts of the metallic poisons are quite soluble in the menstrua employed in extracting the alkaloids and pass into solution with the latter. Previous cases had shown this, one which the writer examined as associate expert, involving the detection of morphine in an embalmed body, very markedly.<sup>1</sup>

In this latter instance, it was of paramount importance that the arsenic extracted in large quantities from the viscera should be separated from the trace of morphine that might coexist, and a prolonged series of extractions was resorted to to eliminate the possibility of mistaking the reactions of the one for the other. This procedure was also necessary to anticipate what was subsequently brought forward by the defence, *viz.*, a point raised by Otto.<sup>2</sup>

The production of arsines and other metallo-organic compounds must also not be lost sight of, for both in testing for organic and inorganic poisons, these exceptionally interesting compounds have been and are likely to be important objects of toxicological research. The fact that evidence of metallic poisons is obtainable from the extractions practised to separate the alkaloids must always be borne in mind, no matter whether the Stas, Erdmann-Uslar or Dragendorff method is employed, or some modification of them, as also when dialysis is resorted to.

Such a course is especially necessary in cases where, in order to recover the very minute quantity of alkaloid that may still remain in a stomach or intestine, the whole of either organ and its contents is submitted to processes for its recovery. Failure to detect an alkaloid may with these precautions in some cases be followed by the finding of an inorganic poison.

It is doubtful whether the method prescribed in many foreign countries, and followed in the laboratory of toxicology in Paris,<sup>3</sup> of comminuting each organ and then mixing together weighed portions of each and of submitting the composite mass to analysis is altogether a wise or safe proceeding. Our own experience is much against it.

<sup>1</sup> People vs. Robt. W. Buchanan, 1600.

<sup>2</sup> Otto: *Ausmittlung der Gifte*, 1884, 117.

<sup>3</sup> Documents du Laboratoire de Toxicologie, Paris, 1897, 23.

The chances of detecting any alkaloid are greatly reduced and the same can be said of metallic poisons. The unequal distribution of poisons through the viscera, and the retention of poisons in certain organs in preference to others, are two of many reasons why a mixture of a fourth of several, say, stomach, intestine, liver, brain, and kidneys, is inadvisable. Nor can there be any hard and fast rule laid down to apply to all cases in the search of poisons. The judgment of the expert must determine in some measure the method to be pursued, and he will naturally have in mind the facts which have been ascertained heretofore, and which have led to the establishment of rules of procedure.<sup>1</sup> No matter what course is followed, it will sometimes happen that important data in regard to the distribution or absorption of the poison detected are unobtainable which could have been secured had the nature of the poison been manifested in the symptoms or indicated by the history of the case. Where, therefore, prominent symptoms are developed, or the autopsy reveals the character of the poison, even if only to so slight an extent as to indicate whether organic or inorganic, narcotic or corrosive, it may best subserve the ends of justice to examine the contents of the stomach apart from the tissue, the gall-bladder and its contents separately from the liver. The fluids of the intestinal tract and the compacted fæces near the rectum separately from each other and the tissue. Much will depend in adopting a course as elaborate as this upon the time that has elapsed since death. A long interment would obliterate to a great degree the clearness of the picture of the distribution of the poison in the body, which we might expect to have developed.

While recent analytical results have tended to show that poisons rapidly diffuse in the body, either when injected post-mortem or imbibed by application to the skin, or though taken in life have afterwards permeated the tissues and reached other organs, we take issue with the claim advanced by the defense in this trial, that toxicology is utterly unable to-day to decide whether a poison extracted from the body has or has not been administered before death.

Though weighable quantities of copper were obtained from the

<sup>1</sup> Dragendorff *Ermittlung von Giften*, 4, 1884.

liver and brain in the case now before us, only traces were found in other organs and in some none at all. Such facts are inexplicable on the basis of post-mortem diffusion. It is therefore of great moment to determine more closely not only the localization of a poison but how intimately it is combined with the tissue. A simple permeation may have taken place, or a definite union or fixation, and such union would often be indicative of vital processes. The employment of suitable solvents will thus lead us to a diagnosis between such true chemical compounds and mere loose impregnations. Tissues are found by the dyer to absorb only certain dyes though they may be transiently stained with others. When in contact with poisons, certain living tissues "dye in the wool."

The alcoholic extracts of stomach, intestines, and liver, were evaporated each by itself and each residue thus obtained treated with strong alcohol and filtered. The new alcoholic extracts now of small volume were again evaporated and their aqueous solutions while still acid treated successively with petroleum ether, benzene, and amyl alcohol. All of these liquids had been especially rectified. After the last amyl alcohol extraction was effected several fresh shakings with petroleum ether were resorted to to remove amyl alcohol from the watery liquid. The aqueous solution was then made alkaline by ammonium hydroxide, and the extractions with petroleum ether and benzene conducted as before. The solution was then acidified, hot amyl alcohol added and emulsified, then enough ammonium hydroxide added to render the solution alkaline. This procedure was repeated often enough to make sure of the extraction of any morphin. Six residues were thus obtained from each of the three viscera. It was a noticeable feature of this case compared to two other investigations made just previously that the residues were of less quantity than in either of the other cases, and that many were indeed so insignificant as to be incapable of purification. Residues I, II and IV were very slight or inappreciable.

Of course, residues VI, from the alkaline liquid extracted by amyl alcohol were submitted to the closest scrutiny. Not only had morphin been prescribed, but it was desirable to ascertain if the ptomaines present might either give or mask the morphin

reactions. After suitable purification they were tested. The morphin reactions were not obtainable, some of the ptomain reactions were pronounced. Minute quantities of morphin solution added to portions of the residues could be detected by appropriate tests. The physiological test of morphin applied to a frog was not obtained. Neither morphin nor other poisonous alkaloid could be identified in any of the residues.

The inorganic poisons claimed attention next. Small quantities of copper arsenite had been prescribed; bismuth also as subnitrate. These metals might therefore be present.

The comminuted tissues, subsequently residues from parts treated for organic poisons, were disintegrated by hydrochloric acid and potassium chlorate. Fresenius and von Babo's method was applied to the stomach first and the results obtained showed the necessity of using the same process with the other organs. A copious precipitate formed the moment hydrogen sulphide was conducted into the faintly acid liquid which had been previously deprived of chlorine by bubbling carbon dioxide through it. The color of the precipitates thus obtained varied with the different organs, but was evidently metallic and not of organic nature. The precaution was taken in the analysis of each separate organ to subject the liquid after saturating it with hydrogen sulphide to warmth and long standing to effect a complete precipitation of the metals.

The precipitates were collected, redissolved in small quantities of hydrochloric acid and potassium chlorate and reprecipitated with previous precautions.

The purified sulphides were washed free of chlorides by dilute hydrogen sulphide water and a separation of the different metals attempted.

It will shorten the story considerably to state that mercury, lead, bismuth, and tin were not detectable in any organ. That zinc was tested for carefully in the filtrate from the hydrogen sulphide and not found.

That antimony and arsenic and in some organs these and copper were separated and identified.

Ammonium sulphide was found to dissolve the washed precipitate entirely or to leave only a small amount of copper sul-

phide. This solution was evaporated and oxidized by nitric acid. Then fused with sodium carbonate and sodium nitrate. When copper was present a dark mass separated. In other cases a white powder was suspended in a clear liquid and all became a white solid on cooling.

At this juncture one of the greatest obstacles was met.

Otto<sup>1</sup> would have us believe that the separation of antimony from arsenic by Meyer's method is as facile and as complete as the destruction of organic matter. He enters into a discussion concerning the methods of manipulation and gives a device for still further preventing dissolved antimony from producing a mirror in the Marsh test by conducting the gases evolved over caustic alkali, a very objectionable process as we shall see later, and comes to the conclusion that the method is reliable.

Notwithstanding all this, the history of this analysis shows first, that when very small quantities of antimony are present they would escape notice when the fused mass is dissolved in water and possesses an *alkaline* reaction as required; secondly, that where much antimony is present it is advisable to resubject the insoluble residue to a second fusion to remove possible traces of arsenic.

The finding of antimony and arsenic in the first organ analyzed, naturally put us on our guard in the testing of others.

Where much antimony was found, there was of course an insoluble white residue, but the brain and muscle contained so little that only the most painstaking work enabled us to detect the antimony and separate it from the arsenic. Since some antimony remains in the Marsh apparatus, the whole not passing out as hydrogen antimonide undiscovered pyroantimoniate may go into solution when the fused mass is dissolved in water and either produce a mirror with arsenic or remain in the generator.<sup>2</sup>

The fact that all the antimony is not converted into gas in the Marsh process renders the use of Hofmann's silver nitrate method unserviceable for the quantitative separation and estimation of antimony and arsenic in toxicological analysis.

While all things considered Meyer's method seems the best

<sup>1</sup> Otto, op. cit., 164.

<sup>2</sup> Dragendorff *Ermittlung der Giften*, Dritte Auflage, 406, 1888.



available, the experiences of this case justify us in cautioning against a too implicit reliance upon it.

The finding of antimony in the stomach was followed by detecting arsenic also. The other organs also revealed the presence of each.

In three viscera, copper was noticeable. The liver yielded 0.0056 gram, the brain and muscle, traces.

The entire quantity of copper extracted from the liver was converted by a small portion of the arsenic obtained from the same organ into copper arsenite and presented as an exhibit along with other portions of the arsenic, there being a great excess of the latter. The absence of copper from the stomach and intestines and its disproportion to the arsenic in the liver and the quantity of each poison found seemed sufficient proof to decide in the negative the question of the copper arsenite prescribed being the source of the arsenic found. Since the copper when found had passed together with antimony and arsenic into the ammonium sulphide solution, then to the fusion, it remained undissolved with the pyroantimoniate and had to be separated from the antimony. This operation followed the incineration of the filters and their contents of sodium pyroantimoniate, in either very small crucibles or porcelain dishes and the fusion of the residues with potassium cyanide. In the case of the intestine the filter was not very small since a considerable amount of sodium pyroantimoniate had been separated. The contents of the filter were removed to a capsule and the filter incinerated. A slight amount of char was left. A drop or two of nitric acid was put on this and heat applied to expel all acid. Whether this was not effectual or some trace of sodium nitrate remained undecomposed is uncertain, but sufficient was left to cause a sharp explosion when the fusion with potassium cyanide was quite well under way, projecting most of the unfused mass out of the dish. While the presence of antimony in large quantity in the intestinal tract was still clearly demonstrated from the residue left in the dish, a quantitative determination of the whole was out of the question. Otto alludes to the possibility of such an explosion in connection with Fresenius and von Babo's method of obtaining arsenic by reduction with potassium cyan-

ide and sodium carbonate, and very naively says "Mir ist bei sorgfaeltigem Arbeiten nie Derartiges vorgekommen."

Although great care was exercised, the accident did happen in the above instance and though the filter ash of the antimonial precipitates from other viscera were in one or two cases similarly treated without the slightest trouble, we caution against the use of nitric acid or an insufficient washing of the pyroantimoniate.

Antimony was weighed either as metal in powder or on platinum, as sulphide or as tetroxide,  $\text{Sb}_2\text{O}_4$ .

Arsenic was weighed either as mirror obtained by the Marsh test or as sulphide. Two mirrors of arsenic were estimated baroscopically.

Organ.	Weight in grams.	Antimony weighed as grams.	Antimony calculated to grams.	Antimony calculated as tartar emetic.
Stomach and contents....	130	Sb 0.0307	0.03070	0.08404
Intestines and contents }	898	Sb 0.0042		
	47	$\text{Sb}_2\text{S}_3$ 0.0072	0.00936	0.02562
Liver, spleen, and fluid }	988			
from abdomen. }	?	$\text{Sb}_2\text{O}_4$ 0.1442	0.11423	0.31314
Heart .....	224	$\text{Sb}_2\text{O}_4$ 0.0028	0.00221	0.00605
Kidneys .....	315	.....	.....	.....
Brain .....	820	$\text{Sb}_2\text{O}_4$ 0.0003	0.000237	0.00065
Muscle .....	227	$\text{Sb}_2\text{O}_4$ 0.0004	0.000317	0.00086
			0.157054	0.43036
equivalent to 6.64 grains.				

Organ.	Weight in grams.	Arsenic weighed as grams.	Arsenic calculated to As.	Arsenic calculated to $\text{As}_2\text{O}_3$ .
Stomach and contents....	130	$\text{As}_2\text{S}_3$ 0.0063	0.00384	0.00507
Intestines and contents }	898	$\text{As}_2\text{S}_3$ 0.1888	0.11512	0.15196
	47			
Liver, spleen, and fluid }	988	$\text{As}_2\text{S}_3$ 0.1134	0.06914	0.09127
from abdomen }	?			
Heart .....	224	As 0.0003	0.00030	0.000396
Kidneys .....	315	As 0.0580	0.05800	0.07656
Brain .....	820	As 0.0002	0.00020	0.000264
		estimated.		
Muscle .....	227	0.0001	0.00010	0.000132
		estimated.		
			0.24670	0.325652
equivalent to 5.02 grains.				

It was deemed important to produce evidence before the jury to confirm the statement that both antimony and arsenic existed in the viscera of the body exhumed. To this end the antimonial and arsenical compounds isolated from the several viscera were brought into weighable form. After weighing, these compounds were submitted to special tests, the results of which in many in-

stances were reserved as *corpora delicti*. These consisted in the case of

*The Stomach* of antimony as metal from the cyanide fusion ; antimony on platinum and on tin ; the oxide and the sulphide.

Bunsen tests, metal, sulphide, and reaction of oxide with silver nitrate and ammonia.

The arsenic was shown as a mirror obtained by Fresenius and von Babo's method. (No antimony could be detected in the fused mass of cyanide.) Arsenious sulphide and silver arsenate were also presented as exhibits.

*The Intestine.* Antimony was shown as metal on platinum and as sulphide ; arsenic as Marsh test mirror and oxide ; also the resulting mirror of a Marsh test using electrolysis ; further, a Reinsch deposit on copper and a sublimate of arsenious oxide therefrom ; silver arsenite, copper arsenite, arsenious sulphide, silver arsenate, magnesium ammonium arsenate and Bettendorff's test with stannous chloride.

*The Liver, Spleen, and Fluid.*—Antimony was shown by Marsh test, metal, silver antimonide and oxide ; deposit from hydrogen antimonide on potassium hydroxide ; antimonious sulphide, antimonious oxide, antimonious oxychloride, the metal on platinum and on tin ; Bunsen's flame tests, metal and sulphide ; Reinsch's test, metal and sublimate.

Arsenic, by Marsh test, elementary and oxide ; deposit made from passing hydrogen arsenide over potassium hydroxide ; silver and copper arsenates.

*The Heart and Blood.*—Antimony was shown as metal and sulphide ; arsenic, as Marsh mirror.

*The Brain.*—Antimony was shown as sulphide ; arsenic, as Marsh mirror.

*The Muscle.*—Antimony was shown as sulphide ; arsenic, as Marsh mirror.

The Marsh test was conducted with the usual precautions and using zinc, slightly platinized, and sulphuric acids of varying strengths.

The apparatus was modeled after that proposed by Prof. R. Ogden Doremus, in 1859, and used in the trial of *The People vs. James Stephens*, since which date no other case of criminal poisoning by arsenic has been tried in New York City, until the

one now under consideration. At a subsequent date, 1878, the same observer, made another change during an investigation of a case where attempt to poison by antimony was charged, *viz.*, The People of the State of New Jersey vs. Rev. Geo. B. Vosburgh. Dragendorff's statement of the decomposability of hydrogen antimonide by stick potassium hydroxide was then verified, but his other statement that hydrogen arsenide does not undergo change was then disproved. This observation has been corroborated by Johnson and Chittenden<sup>1</sup> and in this case.

Dragendorff,<sup>2</sup> in his fourth edition which has just come to hand, modifies his statement concerning the decomposability of hydrogen arsenide by stick potassium hydroxide and refers to work done by Kühn and Säger in this connection. The quotation in the footnote shows that they were anticipated in this matter by R. Ogden Doremus.

Repeated experiments with various kinds of stick sodium and potassium hydroxides have been made since 1878, and though the darkening by arsenic is not as pronounced as with antimony, there is abundant evidence of it. The stains fade more readily. To avoid the loss of arsenic therefore, it has been customary with us to use fragments of pure caustic lime as a drying agent. These at least show no outward sign of a decomposition of either hydrogen antimonide or arsenide.

A small Erlenmeyer flask, well cooled and having granulated zinc within, had acid and when purged of air acid and suspected liquid fed into it from a stop-cock funnel. The escaping gas was dried by a layer of quick-lime between cotton plugs, and then conducted through several inches of hard glass tubing coiled in a spiral, surrounded by a hood and heated by a strong Bunsen flame. The escaping gas was conducted into a solution of silver nitrate.

A complete decomposition of the hydrogen arsenide occurs, no mirror appearing on a second coil, which may be added for precaution. Some of the Marsh tests were conducted with the view of weighing the mirrors, which was done except with the brain

<sup>1</sup> Dragendorff, *op. cit.*, 406; Otto, *op. cit.*, 198; Fresenius' System of Quantitative Chemical Analysis; Am. Ed. 1881, p. 782. "Otto and also Dragendorff recommend to pass the gas first over fragments of caustic potassa. We find, however, in accordance with Doremus, that arsenic is arrested by caustic alkali. S. W. J. and R. H. C."

<sup>2</sup> Dragendorff *Ermittelung von Giften*, vierte Auflage, 386 and 410.

and muscle, where they are so small as to render their retention as exhibits of greater importance than the ascertaining of their weight.

In other cases the Marsh test was used as a proof of the assertion that antimony and arsenic had been isolated. This last was particularly the case in the liver tissue, from which considerable quantities of each poison had been separated. A potassium hydroxide tube was therefore inserted instead of the quicklime, and well-defined black deposits obtained not only on the hydroxide but by the heated coil with antimony and arsenic, the antimonial deposit formed by the action of heat being on the side towards the generator, that of the arsenic beyond the heated spiral.

The arsenical deposit on the hydroxide is therefore of special interest.

Wormley<sup>1</sup> and others lay stress on the fact that the arsenical mirror forms beyond the heated portion of glass.

While conducting a Marsh test by the electrolytic evolution of hydrogen a gradual weakening of the current caused a gradually diminishing flow of gas.

A mirror of the character of those of arsenic formed on each side of the heated spiral. That these were both arsenical was proved by their being soluble in sodium hypochlorite solution, as well as from the extreme care taken to separate antimony from arsenic before employing the latter in the Marsh test.

Antimonious oxide occurs not only as valentinite but as prisms in exetele and as octahedra in senarmontite. The latter resembles ordinary arsenious oxide, a beautiful example of isodimorphism.

Just beyond the hottest part of a spiral employed in making a Marsh test for antimony we observed a crystalline deposit. The crystals were transparent octahedra, did not sublime when the tube was heated, and became red when acted on by hydrochloric acid and then ammonium sulphide. We have therefore apparently an instance of antimonious oxide depositing in the usual octahedral form of arsenious oxide.

Where admissable on account of quantity of arsenic or antimony at our disposal, the gases generated in the Marsh test were

<sup>1</sup> Micro-chemistry of poisons, 229, 1885.

conducted through a silver nitrate solution before heating the spirals.

Though a darkening of the liquid was obtained in each instance, no arsenical reaction could be obtained from the liquid where the suspected antimonial solution was being added to the generator, nor antimony from the black deposit, where a supposable arsenical solution was under test. Antimony and arsenic revealed themselves however in the deposits in the former and in the liquid in the latter, a further evidence that a thorough separation of the two poisons had been effected in the analysis.

The statement is made that selenium hydride yields a black stain to glass at the heated portion, the stain remaining black as long as the glass is hot, but becoming invisible or white in character when the glass cools. We have verified this by experiments made with sulphuric acid containing selenium, a kind of acid not difficult to secure nowadays. Indeed, much sulphuric acid sold as chemically pure should be rejected for toxicological work solely on this ground. This dark stain on the glass is quite distinct from the one alluded to by Wormley<sup>1</sup> as due to arsenic in the glass or to the reddish-brown deposit given by selenium hydride when this gas is tested by the Marsh-Berzelius method. In connection with special tests, we desire to draw attention to the great delicacy of the flame tests when conducted by the methods suggested by Bunsen. We have had occasion to use them in a number of toxicological cases with marked success. In the Vosburgh case many of the exhibits shown were obtained with very small quantities of antimony by these means. Specimens of both antimonial and arsenical reactions were obtained in this investigation and formed part of the exhibit. As a rapid method of bedside testing, these reactions are most excellent. A small sliver of mica is a good substitute for asbestos fiber, and the suspected material can be readily introduced into a small reduction flame of either a Bunsen burner or alcohol lamp, while the oxide tests may be secured with the aid of a candle flame. A bit of china is a good substitute for a capsule, and may be used to catch the deposits by either crushing down the flame or holding it a little distance above it. The deposits may then be tested with suitable reagents.

<sup>1</sup> Wormley. *op. cit.*, 319 and 290.

As an adjunct to the Marsh test for arsenic, when a good-sized mirror had been obtained from a portion of the arsenic, extracted from the intestine, the hydrogen apparatus was removed and dry oxygen obtained by electrolysis was slowly passed in the reverse direction to the hydrogen current. The mirror was then gently heated at the side nearest the coil and the current of oxygen drifted the arsenious oxide formed through the first cold portion beyond where beautiful octahedral crystals were formed.

Although the work thus outlined had been conducted with the assistance of Prof. John A. Mandel, who is jointly entitled to any credit belonging thereto, yet to anticipate certain legal quibbles, the District Attorney, Mr. De Lancey Nicoll deemed it expedient to submit a portion of the viscera for analysis to some one entirely unfamiliar with the history of the case. Prof. R. H. Chittenden was therefore requested to make an independent analysis of the kidneys, which resulted in his finding both antimony and arsenic. The former was in unweighable quantities. The arsenical mirrors obtained from the 315 grams of the kidneys weighed 0.0058 grams.<sup>1</sup> Prof. Chittenden then came to New York and together we analyzed the heart, finding antimony and arsenic as previously stated. The results of his analyses of the kidneys made a separate exhibit which he presented before the jury in his direct examination as a witness.

The defense did not dispute the finding of arsenic and antimony but attempted to show the impossibility of determining whether these poisons had not been introduced by some means after death. The medical history of the case, the condition of the body at the autopsy, the results of the pathological examination, and finally those of the chemical analysis were deemed sufficiently conclusive to the minds of the experts for the prosecution, to make special tests to elucidate this claim uncalled for. No testimony was produced by the defense to show that anyone had so introduced the poisons or had a motive to do so.

During the summing up by the defense, one of the jurors suddenly became insane. It was a recurrence of mental aberration

<sup>1</sup> The entire record of the case will be published under the direction of Assistant District Attorney John E. McIntyre.

which was totally unexpected. He had denied ever having had any mental disease when catechised previous to his acceptance as a juror. A second trial was therefore necessary. It resulted in a verdict of imprisonment for life.

The wife of the prisoner was held in custody for many months, but was finally released on her own recognizance. She had presented herself at the insurance offices dressed in appropriate mourning and claiming to be the widow of "Baum." Several of the companies made payments which she accepted.

It is a noteworthy circumstance that the history of antimonial poisoning is so frequently connected with the destruction of lives heavily insured. Taylor,<sup>1</sup> in a monograph, gives some remarkable cases. In some of these a second poison was administered. Though there have been cases where arsenic has been found along with antimony its presence has been due to the impure nature of the antimony. We have not been able to find the record of any case of chronic antimonial poisoning followed by the use of arsenic as a toxic agent.

BELLEVUE HOSPITAL MEDICAL COLLEGE,  
May 10, 1895.

---

[CONTRIBUTIONS FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 4.]

## ACTION OF HYDROCHLORIC ACID GAS UPON SALTS OF THE ELEMENTS OF GROUP V OF THE PERIODIC SYSTEM.

BY EDGAR F. SMITH AND JOS. G. HIBBS.

Received May 3, 1895.

IN a former number of this Journal (*Vol. XI, 578*) we took occasion to call attention to the rather interesting behavior of sodium vanadate, when gently heated in an atmosphere of hydrochloric acid gas. The results obtained by us proved that vanadic acid is entirely expelled from its salt by this means. This behavior naturally suggested a line of investigation, which we hoped to begin at once, but it was not until very recently that we were able to resume the study. The idea as to whether the salts of the acids of other elements of Group V of the Periodic System were similarly transposed by hydrochloric acid gas, or by the gaseous haloid acids in general, constantly obtruded itself.

<sup>1</sup> On Poisoning by Tartarized Antimony. A. S. Taylor, M.D., F.R.S., *Guy's Hospital Reports*, Third Series, 3, 369, 1857.



We accordingly turned to sodium nitrate and submitted it to the action of hydrochloric acid gas, aiding the reaction by a gentle heat. The gas was evolved by dropping concentrated sulphuric acid from a funnel tube into commercial hydrochloric acid. From the evolution flask it passed through an empty bottle and then through sulphuric acid, from which it entered a combustion tube carrying a boat containing the salt to be acted upon. The products of the reaction were conducted into water, contained in a bulb-receiver, to which was attached a small Erlenmeyer flask containing water.

When the gas came in contact with pure sodium nitrate, action set in even in the cold. The salt assumed a brown-yellow color and a yellow liquid condensed in the cooler portion of the combustion tube. On the application of heat this was driven into the receiver. The action was continued for fifteen minutes, after which the boat was allowed to cool in the gas and then transferred to a vacuum desiccator, where it remained for an hour before it was weighed. An examination of its contents revealed the presence of nothing but sodium chloride. That the conversion was quantitative is evident from the following data:

*Experiment 1.*—0.1878 gram of carefully dried nitrate gave 0.1289 gram of sodium chloride, while the calculated quantity of the latter is 0.1290 gram.

*Experiment 2.*—0.3536 gram of nitrate gave 0.2429 gram of chloride, instead of the theoretical 0.2428 gram.

*Experiment 3.*—0.2971 gram of nitrate gave 0.2040 gram of chloride, while the required quantity is 0.2041 gram.

*Experiment 4.*—0.6462 gram of nitrate gave 0.4440 gram of chloride, instead of 0.4439 gram, as required by theory.

In experimenting with phosphates we used pure sodium pyrophosphate. We found that this salt was not affected when subjected to the action just described. Nothing was expelled from it. When sodium pyroarsenate was substituted for the phosphate action did occur; the arsenic was completely volatilized and collected in the water contained in the bulb-receiver. The contents of the latter were carefully poured into a beaker glass and oxidized with a few drops of nitric acid. Later a "magnesiâ mixture" was added to the neutralized solution, which was permit-

ted to stand fifteen hours before the magnesium ammonium arsenate was filtered. It was finally weighed as magnesium pyroarsenate. The contents of the boat were also dissolved and tested for arsenic, but none was found.

*Experiment 1.*—0.3844 gram of sodium pyroarsenate gave 0.3355 gram of magnesium pyroarsenate, instead of 0.3361 gram, the quantity required by theory.

*Experiment 2.*—0.1093 gram of sodium pyroarsenate gave 0.0959 gram of the magnesium salt, instead of 0.0956 gram, the calculated quantity.

In these experiments a colorless liquid collected in the cooler portions of the tube beyond the boat, but this disappeared upon the application of a gentle heat.

In a third trial the aqueous arsenic solution was not oxidized, consequently the arsenic obtained by precipitation with the "magnesia mixture" was far from the required quantity. From this we infer that the arsenic is not volatilized wholly as a derivative of its higher oxide. The latter doubtless suffers partial reduction. We are striving at present to ascertain in what form it is removed. When it is considered that vanadic acid is expelled as an oxychloride, analogy would suggest some similar form for the arsenic. Of this, however, we expect to speak more definitely in the future.

Care should be exercised in heating the sodium pyroarsenate in the hydrochloric acid gas, as the salt when heated in it fuses very readily, and after fusion sets in the acid acts rather slowly. Magnesium pyroarsenate and lead arsenate were found to be converted quite as readily, by the gas, into their chlorides and the arsenic as completely eliminated as in the case of the sodium salt. The corresponding phosphates remained unchanged.

The separation of the two acids, when associated as sodium salts, as magnesium salts, and lead salts, was tried.

*Experiment 1.*—A mixture, consisting of one-tenth gram of sodium pyroarsenate and an equal amount of sodium pyrophosphate, was treated as just described. The arsenic found in the bulb-receiver and weighed as magnesium pyroarsenate, was 0.0869 gram. Theory required 0.0874 gram. The phosphate remaining in the boat was dissolved in water and the acid finally

weighed as magnesium pyrophosphate. It equaled 0.0830 gram instead of 0.0834 gram, the theoretical quantity.

*Experiment 2.*—In this trial 0.1100 gram of each salt was used. The volatilized arsenic, weighed as pyro-salt, equaled 0.0957 gram, instead of 0.0961 gram. The non-volatilized phosphorus, weighed in the same form, equaled 0.0909 gram, instead of the theoretical 0.0918 gram.

We next prepared magnesium pyroarsenate and magnesium pyrophosphate. Mixtures of these salts were then acted upon by the acid gas. Two separations were made with the following results:

*Experiment 1.*—0.1100 gram of each salt brought into a boat was acted upon by the acid. No difference from the behavior of the sodium salts was observed, excepting that the tendency to fusion was not so marked in this case as with the sodium salts. The volatilized arsenic acid gave 0.1094 gram of magnesium pyro-salt, thus falling short of the theoretical amount by 0.0006 gram. The residual magnesium pyrophosphate weighed 0.1105 gram. This approaches the theoretical (0.1100 gram) so closely that the separation must be viewed as complete.

*Experiment 2.*—The same quantities of the two salts were taken in this trial. Instead of 0.1100 gram of pyrophosphate actually taken the found salt equaled 0.1108 gram. The difference between the arsenic salt used and the quantity of it, which was carried out of the mixture by the gas, equaled 0.0009 gram. An examination of the non-volatilized phosphate showed it to be free from arsenic. Lead arsenate was very readily transposed by the acid into lead chloride, and the volatile arsenic derivative.

Lead arsenate.	Obtained.	Lead chloride.	Required.
<i>Experiment 1.</i> —0.2965 gram	gave 0.2746 gram		0.2747 gram.
" 2.—0.3608 "	" " 0.3347 "		0.3343 "

The residual lead chloride was dissolved in water, and the aqueous solution introduced into a Marsh apparatus. Not a trace of arsenic was found in this way. Upon adding a very slight amount of lead arsenate to the solution the mirror and spots of arsenic were almost immediately observed. The complete transposition of this salt induced us to execute a third trial in which we not only weighed the residual lead chloride and

found it satisfactory, but also determined the arsenic which had been volatilized.

Lead arsenate.	Magnesium pyroarsenate.	
	Found.	Calculated.
0.2965 gram gave.....	0.1022 gram.	0.1028 gram.

Two portions of a mineral containing lead, arsenic acid, and phosphoric acid, were exposed to the action of the acid gas. The volatilized arsenic equaled in (a) 10.42 per cent, and in (b) 10.39 per cent. None remained in the residue contained in the boat.

Experiments have not yet been made with antimonates.

Separations of vanadic and arsenic acids from tungstic and chromic acids are now being carried out, and with encouraging results. The action of hydrobromic, hydriodic and hydrofluoric acid in gas form upon vanadates, nitrates, arsenates and phosphates, has received attention with results which will appear later.

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF  
CHEMISTRY. NO. 5.]

### URANIUM OXYNITRIDE AND URANIUM DIOXIDE.

BY EDGAR F. SMITH AND J. MERRITT MATTHEWS.

Received May 31, 1895.

THE action of ammonia upon molybdenyl ( $\text{MoO}_2\text{Cl}_2$ ) and tungstyl ( $\text{WO}_2\text{Cl}_2$ ) chlorides has received attention in this laboratory. To complete the study of Group VI in this direction, uranyl chloride ( $\text{UO}_2\text{Cl}_2$ ) was prepared, placed in a porcelain boat and heated in a glass tube in a current of dry ammonia. At a comparatively moderate temperature the material began to take on a dark color, and copious fumes of ammonium chloride were evolved. The heat was raised and continued until the ammoniacal salt was no longer produced. The residue was dull black in color. When fused in a nickel crucible with caustic potash, ammonia was slowly evolved. A portion of the substance introduced into aqueous silver nitrate caused the separation of a beautiful deposit of brilliant crystals of metallic silver. Chlorine was not found in the compound. When it was heated with sulphuric acid (1:2) in a sealed tube, complete solution ensued. Upon titration with standardized potassium permanganate, the presence of 6.83 per cent. of dioxide was disclosed. No hydro-

gen was discovered in the material examined for it. Four analyses were made and resulted as follows:

0.2311	gram of material gave	84.81	per cent.	uranium.
0.3139	" " " "	2.19	" "	nitrogen.
0.2412	" " " "	84.87	" "	uranium.
0.1868	" " " "	2.24	" "	nitrogen.

The mean of the uranium and nitrogen determinations was 84.84 per cent. uranium and 2.21 per cent. nitrogen, leaving a difference of 12.95 per cent. for oxygen. The formula we have deduced from these figures is  $U_{11}N_2O_{22}$ , which requires 84.88 per cent. uranium, 2.25 per cent. nitrogen, and 12.87 per cent. oxygen.

Uhrlaub<sup>1</sup> mentions an oxynitride of uranium which from its analysis approximates the formula  $U_8N_2O_{11}$ .

From further experiments made by us it is evident that these oxynitrides are bodies of extremely variable constitution, dependent upon the temperature and length of time to which the uranium body is exposed to the action of the ammonia. This conduct was also observed to prevail with the corresponding derivatives of both molybdenum and tungsten.

*Preparation of Uranium Dioxide.*—The preparation of this compound has been the subject of much discussion. It will be remembered that this is the oxide long looked upon as metallic uranium. Zimmermann<sup>2</sup> found that it resulted upon merely heating the oxide  $U_3O_8$  in indifferent gases, such as carbon dioxide. Others have recommended the ignition of urano-uranic oxide in hydrogen, or together with sulphur, or with sulphur and ammonium chloride. We submit the course by which we obtained it. The oxide  $U_3O_8$  was intimately mixed with a large excess of dry ammonium chloride in a porcelain crucible, and this then placed in a larger Hessian crucible and surrounded with closely packed charcoal. The crucibles were heated in a wind furnace at almost a white heat for about six hours. A reddish brown substance remained. It contained no nitrogen or chlorine. Two portions of it were dissolved in nitric acid and the uranium determined with these results: 88.23 per cent. and

<sup>1</sup> Verbindungen einiger Metalle mit Stickstoff, Göttingen, 1859.

<sup>2</sup> Annalen, 232, 283.

88.00 per cent., giving as a mean 88.12 per cent. A third portion, weighing 0.3363 gram, was heated for fifteen minutes over a Bunsen flame; the increase in weight was 0.0119 gram, and heating again for forty-five minutes there resulted an alteration of only 0.0011 gram, after which the weight continued constant. The total increase of the material taken by its conversion into urano-uranic oxide, was therefore 0.0130 gram, while the calculated increase should be 0.0132 gram.

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF  
CHEMISTRY. NO. 6.]

### THE SEPARATION OF IRON FROM BERYLLIUM.

BY ELIZABETH A. ATKINSON AND EDGAR F. SMITH.

Received May 31, 1895.

THIS separation is generally effected through the solubility of beryllium hydroxide in ammonium carbonate. It is, however, not always satisfactory, and any method affording better results will be of interest to the analyst.

Ilinski and v. Knorre<sup>1</sup> called attention to the use of nitroso- $\beta$ -naphthol in analytical work. For example, they separated cobalt from nickel and iron from aluminum by means of this reagent. Inasmuch as their study has not been continued, it seemed to us of interest to ascertain whether or not the same reagent could be used for the separation indicated at the head of this communication. We used the following solutions: (1) a fifty per cent. acetic acid solution of the nitroso- $\beta$ -naphthol, (2) a ferric solution of which ten cubic centimeters contained 0.1278 gram of ferric oxide, and finally a beryllium chloride solution of which ten cubic centimeters contained 0.1248 gram.

The first step taken was to learn how completely the iron was precipitated by the proposed reagent. To this end ten cubic centimeters of the ferric solution ( $=0.1278$  gram  $\text{Fe}_2\text{O}_3$ ) were diluted with two hundred cubic centimeters of distilled water, and one hundred and twenty-five cubic centimeters of the nitroso- $\beta$ -naphthol added to the cold liquid, which was then allowed to stand for a period of twenty-four hours. The iron precipitate was then filtered out, washed at first with fifty per cent. acetic acid, and subsequently with water, until a few drops of the washings left no residue upon evaporation and ignition upon a strip

<sup>1</sup> *Ber. d. chem. Ges.*, 18, 699, 2728.

of platinum. After the iron nitroso- $\beta$ -naphthol had dried it was mixed with an equal amount of pure oxalic acid, and the filter folded up over the mixture, which was then carefully heated in a weighed porcelain crucible. The heat at first was moderate, but gradually increased until all the carbon had been burned off. These are practically the precautions which were recommended by Ilinski and v. Knorre, so that our experience corroborates that given by these chemists.

The results obtained by us are:

1. 0.1277 gram of ferric oxide.
2. 0.1283 " " " "
3. 0.1277 " " " "

The theoretical ferric oxide equaled 0.1278 grams.

Upon treating ten cc. of the beryllium solution just as described under the iron, no evidence of precipitation was observed even after the expiration of forty-eight hours.

The real object of our study was the separation of the iron from the beryllium. In following out this idea we proceeded in the following manner: Ten cc. of the ferric salt (= 0.1278 gram of ferric oxide) and an equal volume of the beryllium solution, equal to 0.1248 gram beryllium oxide, were diluted to two hundred cc. with distilled water. The nitroso- $\beta$ -naphthol solution was added to this cold mixture. After standing twelve hours the ferric compound was filtered out and disposed of as above described. The ferric oxide found was:

1. 0.1277 gram,
2. 0.1275 " "
3. 0.1277 " "

instead of the theoretical 0.1278 gram.

Efforts made to precipitate uranium salts with this reagent resulted negatively. The substitution of an alcoholic for an acetic acid solution of the reagent made no difference.

We also found that nitroso- $\beta$ -naphthol does not precipitate solutions of cerous salts, of lanthanum ammonium nitrate, of praseodymium nitrate, of neodymium nitrate, of terbium, of erbium, or of sodium molybdate or tungstate. Zirconium chloride gave an orange-colored precipitate, and ceric ammonium nitrate a bright scarlet, flocculent precipitate, which was, however, far from being complete.

# ON THE VAPOR-TENSIONS OF MIXTURES OF VOLATILE LIQUIDS.

BY C. E. LINEBARGER.

[Continued from page 652]

TABLE VII.

*Vapor-Tensions of Mixtures of Toluene and Chloroform at 34.8°.*

*Vapor-Tension of Toluene at 34.8° is 46.8 mm. of Mercury.*

*Vapor-Tension of Chloroform at 34.8° is 289.2 mm. of Mercury.*

Molecules CHCl <sub>3</sub> in 100 mole- cules of liquid mixture.	Molecules CHCl <sub>3</sub> in 100 mole- cules of gaseous mixture.	Grams CHCl <sub>3</sub> in vapor.	Grams C <sub>7</sub> H <sub>8</sub> in vapor.	Ten- sion of CHCl <sub>3</sub> in mm.	Ten- sion of C <sub>7</sub> H <sub>8</sub> in mm.	Vol- ume of air in cc.	Barom- eter in mm.	Inter- nal pressure in mm.
28.74	65.29	0.4856	0.1994	64.7	34.4	1040	747	24
60.43	89.20	1.3578	0.1270	160.9	19.5	1031	754	23

TABLE VIII.

*Vapor-Tensions of Mixtures of Benzene and Carbon Tetrachloride at 34.8°.*

*Vapor-Tension of Benzene at 34.8° is 145.4 mm. of Mercury.*

*Vapor-Tension of Carbon Tetrachloride at 34.8° is 169.4 mm. of Mercury.*

Molecules CCl <sub>4</sub> in 100 mole- cules of liquid mixture.	Molecules CCl <sub>4</sub> in 100 mole- cules of gaseous mixture.	Grams CCl <sub>4</sub> in vapor.	Grams C <sub>6</sub> H <sub>6</sub> in vapor.	Ten- sion of CCl <sub>4</sub> in mm.	Ten- sion of C <sub>6</sub> H <sub>6</sub> in mm.	Vol- ume of air in cc.	Barom- eter in mm.	Inter- nal pressure in mm.
7.21	9.66	0.1741	0.8260	14.5	135.4	1205	762	18
18.68	20.54	0.3931	0.7561	32.5	125.5	1205	758	20
28.00	35.71	0.6267	0.5730	60.0	105.0	1016	756	12
50.19	55.03	1.1231	0.4666	91.3	75.6	1201	762	19
63.88	65.27	1.2699	0.3431	103.1	54.5	1219	760	27
77.89	83.01	1.5321	0.1669	117.6	31.8	1034	754	26

TABLE IX.

*Vapor-Tensions of Mixtures of Toluene and Carbon Tetrachloride at 34.8°.*

*Vapor-Tension of Toluene at 34.8° is 46.8 mm. of Mercury.*

*Vapor-Tension of Carbon Tetrachloride at 34.8° is 169.4 mm. of Mercury.*



# VAPOR-TENSIONS OF MIXTURES OF VOLATILE LIQUIDS. 691

Molecules CCl <sub>4</sub> in 100 mole- cules of liquid mixture.	Molecules CCl <sub>4</sub> in 100 mole- cules of gaseous mixture.	Grams CCl <sub>4</sub> in vapor.	Grams C <sub>7</sub> H <sub>8</sub> in vapor.	Ten- sion of CCl <sub>4</sub> in mm.	Ten- sion of C <sub>7</sub> H <sub>8</sub> in mm.	Vol- ume of air in cc.	Barom- eter in mm.	Inter- nal pressure in mm.
30.69	58.19	0.4754	1.2046	51.5	37.0	1016	756	12
53.85	67.86	0.9305	0.1260	78.3	22.3	1022	758	17
60.00	83.67	0.9624	0.1126	99.1	19.4	1020	759	14
91.87	97.22	1.6063	0.0281	155.1	4.5	1017	756	13

TABLE X.

*Vapor-Tensions of Mixtures of Nitrobenzene and Carbon Tetrachloride at 34.5°.*

*Vapor-Tension of Nitrobenzene at 34.8° is 1.16 mm. of Mercury.*

*Vapor-Tension of Carbon Tetrachloride at 34.8° is 169.4 mm. of Mercury.*

Molecules CCl <sub>4</sub> in 100 mole- cules of liquid mixture.	Molecules CCl <sub>4</sub> in 100 mole- cules of gaseous mixture.	Grams CCl <sub>4</sub> in vapor.	Grams C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> in vapor.	Ten- sion of CCl <sub>4</sub> in mm.	Ten- sion of C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> in mm.	Vol- ume of air in cc.	Barom- eter in mm.	Inter- nal pressure in mm.
5.37	93.51	0.3095	0.0175	18.9	1.3	1973	760	20
50.73	94.47	1.1111	0.0489	113.9	6.2	1020	756	12
73.54	96.09	1.4420	0.0471	141.5	5.6	1022	753	18
95.21	98.61	1.7798	0.0190	167.6	2.3	1024	753	18

## 10. INFLUENCE OF TEMPERATURE ON THE VAPOR-TENSIONS OF MIXTURES OF VOLATILE LIQUIDS.

It is a well-known fact that the higher the temperature the greater the vapor-tension; this is true of mixtures of liquids as well as of the liquids themselves. It may be, now, that the vapor-tensions of mixtures of volatile liquids exhibit a deportment varying with the temperature; but if it can be shown that change of temperature is without influence upon the nature of the phenomenon presented by the vapor-tensions of such mixtures, the experimental investigation of the subject is much simplified, for theoretic conclusions based on data found at a certain temperature can be at once applied to other temperatures, so that the investigation of the vapor-tensions of mixtures of various concentrations at one temperature suffices for the discussion and elucidation of the entire problem. Material which furnishes an answer to the question as to whether temperature has an influence upon the vapor-tensions of mix-

tures of volatile liquids can be found in the papers of Regnault (*loc. cit.*), Raoult (*loc. cit.*), and Brown (*loc. cit.*).

Regnault's determinations were made through a considerable range of temperature, and, although, at most only three different concentrations were examined, it is possible by rearranging them to get an answer to our query. The mixtures which can be utilized are five in number,—two mixtures of carbon bisulphide and ethyl oxide, whose vapor-tensions were determined by the static method, and one mixture of the same liquids, the vapor-tension of which was determined by the dynamical method; and two mixtures of carbon bisulphide and carbon tetrachloride of which the vapor-tensions were investigated by the static method.

The first mixture of carbon bisulphide and ether was made up of sixty-two volumes of the first liquid and thirty-eight volumes of the second, ("Mélange de 62 sulphure de carbone et 38 d'éther, en volumes"), and eleven determinations of its vapor-tension were made in the temperature interval  $4.72^{\circ}$  to  $39.44^{\circ}$ . If we put the specific gravity of Regnault's carbon bisulphide at 1.27, and that of his ether at 0.78, the mixture contained by weight 27.35 per cent. of ether, and 72.65 per cent. of carbon bisulphide; or a hundred molecules of the mixture contained 27.20 molecules of ether and 72.80 molecules of carbon bisulphide. The second mixture was prepared by mixing fifty-six volumes of ether and forty-one volumes of carbon bisulphide ("Mélanges de 56 éther et de 41 sulphure de carbone en volumes"). Thirteen determinations were made of the vapor-tensions of this mixture at temperatures varying from  $8.01^{\circ}$  to  $38.18^{\circ}$ . One hundred parts by weight contained then 45.61 parts of ether and 54.39 parts of carbon bisulphide; and one hundred molecules of the mixture contains 46.29 molecules of ether and 53.71 molecules of carbon bisulphide.

The third mixture of carbon bisulphide and ether was made up of equal volumes of each; ("Mélange, a volume éguax, de sulphure de carbon et d'éther") about twenty-five measurements were made in the temperature interval from  $20.81^{\circ}$  to  $121.48^{\circ}$ . The percentage composition of the mixture is 61.95 per cent. of carbon bisulphide and 38.05 per cent. of ether, and the molecu-

lar percentage composition is 61.32 molecules of carbon bisulphide and 38.68 molecules of ether.

The first mixture of carbon tetrachloride and carbon bisulphide contained equal volumes of the two liquids; ("Mélange de volumes égaux de chlorure de carbone et de sulphure de carbone") ten determinations of its vapor-tension were made at temperatures varying from  $8.75^{\circ}$  to  $48.43^{\circ}$ . If we put the specific gravity of Regnault's carbon tetrachloride as equal to 1.62, and that of his carbon bisulphide as equal to 1.27, the percentage composition by weight of the mixture is 56.06 per cent. of carbon tetrachloride and 43.94 per cent. of carbon bisulphide; and one hundred molecules of the mixture contain 61.2 molecules of the first-named liquid and 38.8 molecules of the last-named.

In indicating the composition of the second mixtures Regnault uses the following words: "Mélange de 60 parties sulphure de carbone et de 145 chlorure de carbone." There is doubt here as to whether Regnault means by "parties," parts by weight or by volume. This is the only place where this form of expression is used, and in the other cases, it is expressly stated that the units of measure are volumes. I take it, then, that in this case parts by weight are to be understood, and in the sequel it will be seen that the regularity of the data as represented graphically renders this understanding of the matter warranted. At any rate, the difference between the results of calculations with volumes or weights as bases is not very great, so that there is not much danger of committing any very gross error. By weight the percentage composition of this mixture is 70.73 per cent. of carbon tetrachloride and 29.27 per cent. of carbon bisulphide, while one hundred molecules of it contain 65.47 molecules of carbon tetrachloride and 34.53 molecules of carbon bisulphide. I give also the percentage molecular composition on the assumption that Regnault's "parties" means parts by volume; one hundred molecules of the mixture contain 54.47 molecules of carbon tetrachloride and 45.53 molecules of carbon bisulphide.

In order to transform Regnault's data, the following procedure was gone through with: In a system of coordinates with temperatures as abscissas and vapor-tensions as ordinates, his measurements were plotted on a large scale; as might be expected

of any of Regnault's experimental work, the points fell very close to a regular curve. At points at this curve corresponding to  $0^{\circ}$ ,  $10^{\circ}$ ,  $20^{\circ}$ ,  $30^{\circ}$ , etc., the value of the ordinates was carefully taken, that is, the vapor-tensions for each of the above temperatures. In this way data were obtained by means of which isothermal curves were drawn in a system of coordinates with concentrations as abscissas and vapor-tensions as ordinates.

An inspection of the isothermal curves shows that no appreciable influence of temperature manifests itself; the vapor-tension of the more volatile component of the mixture increases, indeed, more rapidly than that of the less volatile, but this does not affect the contour of the curve, its inclination alone being somewhat altered.

Raoult<sup>1</sup> made a special study of the possible influence of temperature upon the vapor-tensions of mixtures of ether with each of the following liquids almost nonvolatile at low temperatures: turpentine, aniline, perchlorethane, and benzoic acid, the temperature interval being from  $0^{\circ}$  to  $22^{\circ}$ . The results of his experiments permitted him to draw the definite conclusion that in the above temperature interval the vapor-tension is quite independent of the temperature.

The experiments of Brown<sup>2</sup> on the boiling-points of carbon bisulphide and carbon tetrachloride may be brought forward as evidence that the influence of the temperature on the vapor-tensions of mixtures of normal liquids is very slight; he found the curves, sketched with percentage composition on the axis of abscissas, and boiling-points on the axis of ordinates, for the pressures 747 to 760, and 430 to 432 mm. to be practically parallel.

From the above considerations, we may conclude that temperature has but a vanishing influence upon the vapor-tensions of mixtures of normal liquids; that is to say, although the higher the temperature, the greater the vapor-tension, the regularities found and the laws deduced from observations made at any one temperature are, without question, applicable to any other temperature, which, however, be it remarked as a caution, should probably not be too different from that of the observations.

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Loc. cit.*

XI. RELATIONS BETWEEN THE VAPOR-TENSIONS, PARTIAL  
AND TOTAL, AND THE CONCENTRATION OF THE  
LIQUID PHASES.

We remark first, that the tension of the mixed vapor emitted by any of the mixtures of volatile liquids examined is always greater than the tension of the less volatile liquid and always less than that of the more volatile liquid; also, that the partial tension or pressure of either component, of any mixture, is always less than the vapor-tension of the component in a state of purity;<sup>1</sup> these two properties belong to all the mixtures investigated. In the discussion of the other properties, we shall find it convenient to divide the mixtures into classes. In the first class we put the mixtures of benzene and toluene with monochlor- and monobrombenzene; in the second, the mixtures of chloroform with benzene, and with toluene; in the third, the mixtures of carbon tetrachloride with toluene, and with benzene; and in the fourth and last, the mixture of nitrobenzene and carbon tetrachloride.

Now the mixtures of the first class are made up of liquids which are very similar in their chemical constitution, and it is natural to expect that they will exhibit the very simplest phenomena when mixed with one another. And, indeed, this expectation is realized, for the vapor-tensions of their mixtures are seen to be linear functions of the concentration: in the graphic representations (abscissas = molecular percentages; ordinates = vapor-tensions) of the determinations, these fall upon, or very close to the straight lines connecting the points on the axes of ordinates corresponding to the vapor-tensions of each of the pure liquids. In order to find the vapor-tension of any mixture of these liquids, all that is necessary to do is to connect on the axis of ordinates, the points representing the vapor-tensions of the two liquids in a state of purity, by a straight line, and where the perpendicular to the axis of abscissas cuts this line, the value of the ordinate corresponding to the point of intersection gives

<sup>1</sup> This observation does not seem to be confirmed in the case of the partial pressure of nitrobenzene in its mixture with carbon tetrachloride. This exception, however, I am inclined to attribute to experimental errors, which made themselves particularly felt in the investigation of mixtures of these two liquids. Indeed, if the allowance be made for the degree of accuracy which we have decided the method capable of yielding, it will be seen that the discrepancy can be made to disappear almost entirely.

the vapor-tension of the chosen concentration; of course, partial tensions can be found in a similar way. Also, by the application of the "rule of mixtures," it is easy to calculate the total or partial tensions. It may be worth while to remark, in passing, that these four liquids, which we have put in a class by themselves, are just those which verify by far the best the generalizations of van der Waals; undoubtedly, these liquids are to be reckoned as in the highest degree "normal," as their behavior approaches most nearly that theoretically predicted.

In the second of our classes we find a different behavior. When chloroform is added to benzene or to toluene, the total vapor tension is less than that resulting from the calculation by the rule of mixtures; the variation reaches a maximum when 100 molecules of the mixture contain from fifty to sixty molecules of chloroform; the curve then tends to approach the straight line connecting the points on the axis of ordinates representing the vapor-tensions of the pure liquids, practically coinciding with it when the number of chloroform molecules has passed eighty. The depression of the vapor-tension of chloroform, caused by the addition of either benzene or toluene, is linearly proportional to the concentration only in solutions containing less than twenty molecules of either hydrocarbon to 100 molecules of the mixture.

When we consider the partial tensions of these mixtures, we see that the same regularity as was observed in the first class of liquids is found here, but only for toluene and benzene; the partial tension curve for chloroform resembles closely in its contour that for the total tension of the mixture. The departure of chloroform from the straight line is not, however, very marked.

In the third class of mixtures, we meet with a different behavior. When benzene or toluene is added to carbon tetrachloride, we observe that the curve of total tension follows closely the line connecting the points corresponding to the vapor-tensions of the mixed liquids until towards the abscissas value of eighty; the curve then commences to fall, only to rise again, and pass above the straight line, when, finally, it changes its direction to fall upon the axis of ordinates at the point standing for the vapor-tension of the pure hydrocarbon, benzene, or

toluene, as the case may be. As is seen, the curve has three turning points. The curve of the partial tension of the carbon tetrachloride resembles in every detail, in each mixture, that of the total tension; but once more it is observed that the partial pressure curve for the hydrocarbons is, so to say, a straight line. It is truly a remarkable result that in the mixtures which have such different total tension curves, the curve for these two liquids should turn out so simple. There is but little doubt that the above instances are sufficient to render very probable the assumption that this behavior is general, and that in all binary mixtures made up of benzene or toluene, with any other volatile liquid whatsoever, the same normality in the behavior as regards partial vapor-tension of these two hydrocarbons will be found. It is even possible to go a step farther, and claim that, inasmuch as in the mixtures of the first class, normality of the partial pressure was found in the case of each component of the mixture, this normality will persist in mixtures of the halogen compounds of benzene with any other liquids.

The fact that benzene and toluene possess "straight line" partial pressure curves will enable us to get reliable and important information as to the partial pressures of other liquids mixed with either of the hydrocarbons, from a knowledge of the total pressure of the mixtures; for all that is necessary to do is to draw, in the coordinate system adopted in this paper, the total pressure curve and a straight line from the point, representing, on the axis of ordinates, the vapor-tension of benzene at the temperature at which the determination has been made, to the foot of the opposite ordinate; the value of any ordinate comprised between these two curves gives, then, the partial pressure, to a very close approximation, of the other component of the mixture.

Furthermore, it is apparent that the partial tensions of either chloroform or carbon tetrachloride is the same when mixed in the same proportions with either benzene or toluene; the simplicity of the behavior of the latter liquids permits of the free exhibition of the peculiarities in that of the former.

The fourth class of mixtures, of which the only representative here is the mixture of nitrobenzene and carbon tetrachloride,

does not, in reality, belong to our subject of investigation, which is to study mixtures of volatile liquids only, and not those of a volatile with an almost involatile one. Still it was thought advisable to find out what the partial tensions of mixtures of such liquids would be, inasmuch as Raoult<sup>1</sup> has made an elaborate study of the total vapor-tension of mixtures of ether and several almost non-volatile liquids. As is seen in the curve, the partial pressure of the carbon tetrachloride and the total pressure of the mixture are almost identical, just as would naturally be expected. The curves are, if we regard the right-hand ordinate first, at the beginning parallel with the straight line connecting the points representing the vapor-tensions of the pure liquids; they then turn upwards, reach a maximum distance from the straight line at about the abscissas value of fifty, and then gradually turn downwards towards the origin. I was curious to see if this behavior was characteristic of the mixtures of liquids investigated by Raoult.

Accordingly, I have recalculated his data so as to get them into a form comparable with mine. These recalculated data are given in the following small tables:

TABLE A.

*Vapor-Tensions of Solutions of Turpentine in Ether at 16.2°.*  
*Vapor-Tension of Turpentine at 16.2° is four mm. of Mercury.*  
*Vapor-Tension of Ether at 16.2° is 377 mm. of Mercury.*

Molecules of turpentine in 100 molecules of solution.	Vapor-tension in mm. of mercury.	Molecules of turpentine in 100 molecules of solutions.	Vapor-tension in mm. of mercury.
5.9	354	35.5	255
12.1	332	47.9	212
23.4	294	64.5	159

TABLE B.

*Vapor-Tension of Solutions of Nitrobenzene in Ether at 16.0°.*  
*Vapor-Tension of Nitrobenzene at 16.0° is four mm. of Mercury.*  
*Vapor-Tension of Ether at 16.0° is 374 mm. of Mercury.*

Molecules of nitrobenzene in 100 molecules of solution.	Vapor-tension in mm. of mercury.	Molecules of nitrobenzene in 100 molecules in solution.	Vapor-tension in mm. of mercury.
6.0	353	56.2	232
17.9	321	75.9	166
35.5	278	84.0	132

<sup>1</sup> *Loc. cit.*



TABLE C.

*Vapor-Tensions of Solutions of Aniline in Ether at 15.3°.**Vapor-Tension of Aniline at 15.3° is four mm. of Mercury.**Vapor-Tension of Ether at 15.3° is 364 mm. of Mercury.*

Molecules of Aniline in 100 molecules of solution.	Vapor-tension in mm. of mercury.	Molecules of Aniline in 100 molecules of solution.	Vapor-tension in mm. of mercury.
3.8	349	20.5	292
7.7	335	49.6	210
14.8	308	68.7	147

TABLE D.

*Vapor-Tension of Solutions of Methyl Salicylate in Ether at 14.2°.**Vapor-Tension of Methyl Salicylate at 14.2° is four mm. of Mercury.**Vapor-Tension of Ether at 14.2° is 306 mm. of Mercury.*

Molecules of methyl salicylate in 100 mole- cules of solution.	Vapor-tension in mm. of mercury.	Molecules of methyl salicylate in 100 mole- cules of solution.	Vapor-tension in mm. of mercury.
1.1	344.6	23.2	281
2.1	343.6	49.0	208
4.8	332.0	77.0	125
9.2	316.0	85.0	101
15.1	301.0	....	....

TABLE E.

*Vapor-Tensions of Solutions of Ethyl Benzoate in Ether at 11.7°.**Vapor-Tension of Ethyl Benzoate at 11.7° is three mm. of Mercury.**Vapor-Tension of Ether at 11.7° is 313 mm. of Mercury.*

Molecules of ethyl ben- zoate in 100 molecules of solution.	Vapor-tension in mm. of mercury.	Molecules of ethyl ben- zoate in 100 molecules of solution.	Vapor-tension in mm. of mercury.
4.9	296	53.0	167
9.6	286	75.5	94
27.1	235	94.4	39

If these results be plotted in a system of coordinates, the curves will be found to have a close resemblance to the one which I have found for the mixture of nitrobenzene and carbon tetrachloride. It seems likely that this form of curve is the general one for the total tension of mixtures of a volatile with an almost fixed liquid.

## XII. RELATIONS BETWEEN THE CONCENTRATIONS IN THE GASEOUS AND LIQUID PHASES.

The relations between the concentration in the gaseous and liquid phases is clearly shown by curves drawn in a system of coordinates, of which the axis of abscissas is taken for the rep-

resentation of the molecular percentage composition of the liquid phase, and the axis of ordinates for that of the gaseous phase. In Fig. V are drawn these curves, the data being taken from the first two columns of tables.

As is seen, the curves prove to be very regular, and group themselves on either side of the diagonal of the square, according as the component chosen to increase from left to right in the diagram is more or less volatile than the other; as this was taken to be the component containing a halogen, the curve is below the straight line when the halogen-containing liquid is less volatile than the other, and above, when it is more volatile.

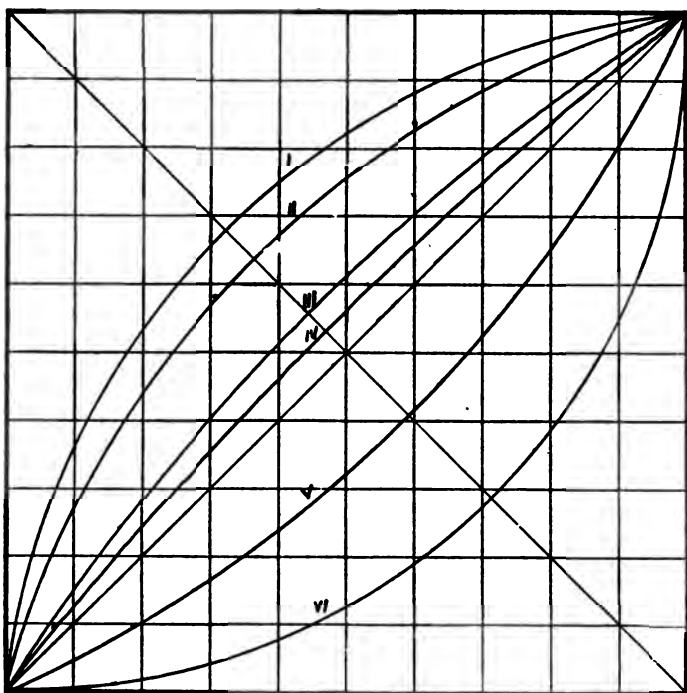


FIG. 5.—RELATIONS BETWEEN THE CONCENTRATIONS IN LIQUID AND GASEOUS PHASES.

Abcissas = molecules of one liquid in 100 molecules of mixture of liquids.  
Ordinates = molecules of one vapor in 100 molecules of mixture of vapors.

- Curve I.....Toluene-chloroform.  
" II.....Toluene-carbon tetrachloride.  
" III.....Benzene-chloroform.  
" IV.....Benzene-carbon tetrachloride.  
" V.....Toluene-monochlorbenzene.  
" VI.....Benzene-monochlorbenzene.

Furthermore, the greater the difference in the volatility of the two liquids in the mixture the greater the curvature. It is very probable that mixtures of two normal liquids with the same vapor tension would give off vapors with identical composition in both liquid and gaseous state.

#### XIV. HEAT OF DILUTION AND SOLUTION. IDEAL CONCENTRATED SOLUTIONS.

Kirchoff<sup>1</sup> developed by thermodynamic considerations an equation showing a relation between the heat of dilution of a solution and its vapor-tension. If we designate by  $dQ$  the heat brought into play when the small quantity  $dm$  of water is added to the solution, and if  $p'$  represent the vapor-tension of the solution and  $p$  that of the pure solvent, while  $T$  is the temperature and  $R$  the gas constant measured in units of heat, he found that

$$(A) \quad \frac{dQ}{dm} = RT^2 \frac{k \log \frac{p'}{p}}{dT}$$

This equation was more particularly developed for the case of solutions of fixed substances, and has in fact been compared with the experiments done on the vapor-tensions and heat of dilution of sulphuric acid dissolved in water. Recently, however, three quite similar formulas have been obtained which apply directly to the heat given out or taken in when two liquids are mixed, and the corresponding changes of the elastic forces of the vapors. LeChatelier<sup>2</sup> developed for the case of a mixture of two liquids the formula

$$(B) \quad n \frac{dp}{p} + n' \frac{dp'}{p'} - 500 \frac{nL_1 + n'L_2 + \lambda}{T^2} dT = 0$$

wherein  $p$  and  $p'$  are vapor-tensions,  $L_1$  and  $L_2$  latent heats of vaporization,  $\lambda$  the heat disengaged on mixing  $n + n'$  molecules of two liquids, and  $T$  is the temperature. As is readily seen, this formula is a special adaptation of Kirchoff's formula; in reality, they may be considered as expressing similar relations.

Nernst<sup>3</sup> by carrying out a closed cycle in the thermodynamic

<sup>1</sup> Ueber einen Satz der Mechanischen Wärmetheorie und einige Anwendungen desselben: *Ann. der Phys. Pogg.*, 103, 177, 1885.

<sup>2</sup> *Loc. cit.*, 281.

<sup>3</sup> *Theor. Chem.*, 102-105.

sense of the term, in which semi-permeable membranes play a conspicuous rôle, has arrived at this equation :

$$(C) \quad Q_{(x)} = -RT^2 \frac{d}{dT} \left( \ln \frac{p_0}{p} + x \ln \frac{P_0}{P} \right)$$

in which  $Q_{(x)}$  is the heat of mixture,—equal to the decrease of the internal energy,— $R$  and  $T$  have the same signification as in formula (A),  $p_0$  and  $P_0$  are the vapor-tensions of the pure liquids, and  $p$  and  $P$  the vapor-tensions at the moment of mixing, and  $x$  the number of molecules of one component to one molecule of the other. As is evident, this formula is quite similar to that of Kirchoff, which, Nernst claims, is but a special case of his more general one.

Duhem<sup>1</sup> has, by the application of the thermodynamic potential, which has proven so fruitful in his hands, developed the following formulas, each of which is applicable to the heat evolved or absorbed when to a solution of two liquids, certain masses, of either liquid,  $\delta M_1$  or  $\delta M_2$ , are added :

$$(D) \quad EL_1 = \frac{4 \Sigma R}{\alpha_1 \omega_1} T^2 \frac{d}{dT} \log \frac{p_1(x, T)}{P_1(T)},$$

$$(D \text{ bis}) \quad EL_2 = \frac{4 \Sigma R}{\alpha_2 \omega_2} T^2 \frac{d}{dT} \log \frac{p_2(x, T)}{P_2(T)};$$

in the formulas  $E$  is the mechanical equivalent of heat ;  $L_1$  and  $L_2$  heats of solution ;  $\Sigma$  the specific volume of hydrogen in normal conditions of temperature and pressure ;  $R$  a constant having the same value for all ideal gases ;  $\alpha_1$  and  $\alpha_2$  atomicities ;  $\omega_1$  and  $\omega_2$  molecular masses,  $T$  the temperature ;  $p_1$  and  $p_2$  the vapor-tensions of the solutions ; and  $P_1$  and  $P_2$  the vapor-tensions of pure liquids. It is at once apparent that this equation, if Duhem's complete, but rather prolix manner of writing be suitably transformed, is identical with the one developed by Kirchoff.

An important conclusion can be drawn from the above equations, in case the heat of solution turns out to be equal to zero ; then,  $\frac{d}{dT} \log \frac{p'}{p}$  becomes equal to zero too, and the ratio  $\frac{p'}{p}$  is independent of the temperature. That, in reality, to a very close

<sup>1</sup> Dissolutions et Mélanges ; Troisième Mémoire ; Les Mélanges Doubles : Travaux et Mémoires des Facultés de Lille, 100, 1894.

approximation such is the condition of affairs for certain dilute solutions has been known since 1857; and such solutions are said to follow the law of von Babo,<sup>1</sup> which says that the heat of dilution must be zero.

Now we have found that the mixtures of the first class at least, that is, those made up of benzene, toluene, monochlor- and monobrombenzene, have vapor-tensions which are practically independent of the temperature, that is, the fraction  $\frac{p'}{p}$  has the same value for all temperatures. It follows then that no thermal change should accompany the act of mixing of the liquids; their heat of solution of dilution is zero. No experiments so far as I know, which can give evidence as to the correctness of this statement, have been performed; but there can be no questioning of the truth of the relation developed and it is not at all probable that the determinations of the vapor-tensions are much in error.

In order to put this prevision of theory to the test of experience, I have made a number of determinations of the thermal effect of mixing liquids, especially those of the first class. Two methods were employed, that requiring the use of a Bunsen's ice-calorimeter, and that depending upon the measurement of the change of temperature.

The ice-calorimeter which was employed was of comparatively large size, the inner tube having an internal bore of twenty mm., and a length of 200 mm. within the outer tube. The calorimeter was filled, set up, and manipulated nearly as recommended by Schuler and Wartha, the amount of mercury absorbed or expelled being weighed.

After the calorimeter had been gotten into normal working condition, it was found that a continuous formation of ice was occurring around the inner tube. The amount was, however, not only slight, but also very constant, so that it was possible to apply an entirely reliable correction for it.

The cooling of the liquids to 0° and their subsequent mixing was accomplished in the following manner: A thin glass tube closed at one end and of such internal diameter as to permit of

<sup>1</sup> *Berichte über die Verhandlungen der Gesellschaft für Beförderung der Naturwissenschaften zu Freiburg in Brisgau.* January, 1857, 282.

its being easily but snugly slipped into the inner tube of the calorimeter was of such length that about an inch of it projected out of the calorimeter. A cylindrical pipette, fitting easily into the glass tube just described, had its lower orifice directly below the bulb, and was closed by means of a glass rod running axially up through the pipette and ground accurately into the orifice; a bit of rubber tubing was slipped over the glass rod, which could be pushed down between the rod and the stem of the pipette, thus closing the latter above. The pipette was held in place in the tube by means of a tightly fitting cork.

A piece of aluminum foil was for about two-thirds of its length cut into in several places along each side nearly to the middle, and the parts thus formed were so bent that, when the other third of the foil was rolled into cylindrical shape and slipped over the lower part of the bulb of the pipette, where it was held by its own elasticity, they formed a number of small paddles, those on one side directed upwards, those on the other directed downwards. Such a stirrer permits of a rapid and complete mixing of liquids.

To make a determination, a certain amount of one liquid is introduced into the pipette and weighed therein. The other liquid is weighed in the tube which is provided provisionally with a cork. The aluminum stirring contrivance is then slipped over the bulb of the pipette, and the latter passed into the tube, being held in place by a tightly fitting cork; the pipette is not pushed deep enough into the tube to have its orifice dip in the mixture of liquids, and the paddles reach to the bottom of the tube. A weighed dish of mercury is allowed to catch the expelled mercury of the empty calorimeter for exactly half an hour before the liquids are introduced; by this means the calorimeter correction just before the determination is obtained. After the introduction of the tube and pipette, the calorimeter is allowed for a half hour or so to get again into its normal state. After this has come to pass, a fresh dish of mercury is put under the mercury tube, the cork holding the pipette is lifted, the glass rod is raised a little, and the liquid in the pipette allowed to run out. The pipette is then tightly closed, and twisted around for a half minute or so to thoroughly mix the two liquids. The cork is

again inserted in the tube, and the whole left for exactly half an hour. At the expiration of that time, the mercury vessels are changed, and the calorimeter left to itself for another half hour, when the mercury vessels are again changed, and the tube and pipette removed. The pipette is again weighed, and the difference between the two weights gives the amount of liquid. The amount of mercury expelled from the apparatus during the last half hour should, if the thermal equilibrium, disturbed by the heat evolved or absorbed by the mixture of the liquids, has reestablished itself, and if no change in the velocity of the freezing of the water itself has supervened, be equal to the amount expelled in the first half hour; in other words, the corrections in each case should be equal. This I found to be invariably the case. The heat effect of the mixing of the liquids is accordingly to be obtained from the excess or deficit of the amount of mercury expelled or absorbed in the next to the last half hour compared with that expelled during the first and the last half hours. This difference divided by 0.01544 gives the number of lesser calories measuring the heat effect of the mixing of the liquids.

By a most scrupulous attention to details in manipulation and to observance of time, as well as to care in weighing, I think that the determinations are exact to one-tenth calorie, and even to less than that.

I give in the following experiments the data obtained in the determination of the thermal effect of mixing such liquids as have been found in the foregoing pages to show the simplest behavior, and have hence been grouped into the first class. The negative sign before a datum is indicative of an absorption of heat, and consequent formation of ice and expulsion of mercury, while the positive sign indicates an evolution of heat etc.

*Experiment 1.*—Heat effect of mixing chlorbenzene and toluene:

Chlorbenzene .....	3.0028 grams.
Toluene .....	4.3032 "
Calorimeter correction in weight of mercury.....	—0.0013 "
Weight of mercury moved .....	—0.0018 "
" " " " due to mixing of liquids .....	—0.0005 "
Thermal effect measured in lesser calories.....	—0.032 "

*Experiment 2.*—Heat effect of mixing chlorbenzene and toluene:

Chlorbenzene .....	3.7715 grams.
Toluene.....	4.2190 "
Calorimeter correction in weight of mercury.....	—0.0014 "
Weight of mercury moved .....	—0.0020 "
" " " " due to mixing of liquids.....	—0.0006 "
Thermal effect measured in lesser calories .....	—0.033 "

*Experiment 3.*—Heat effect of mixing brombenzene and toluene:

Brombenzene .....	4.9530 grams.
Toluene.....	4.3680 "
Calorimeter correction in weight of mercury.....	—0.0009 "
Weight of mercury moved .....	—0.0020 "
" " " " due to mixing of liquids.....	—0.0011 "
Thermal effect measured in lesser calories.....	—0.072 "

*Experiment 4.*—Heat effect of mixing brombenzene and toluene:

Brombenzene .....	1.1611 grams.
Toluene.....	7.3887 "
Calorimeter correction in weight of mercury.....	—0.0010 "
Weight of mercury moved .....	—0.0005 "
" " " " due to mixing of liquids.....	+0.0005 "
Thermal effect measured in lesser calories.....	+0.032 "

Inasmuch as benzene solidifies at a temperature somewhat above that of melting ice, was not possible to carry out determinations in the ice-calorimeter with it in the pure state; accordingly I prepared a mixture containing 97.37 per cent. benzene and 2.63 per cent. chlorbenzene, which was used in experiment five.

*Experiment 5.*—Heat effect of mixing benzene and chlorbenzene:

Mixture of benzene and chlorbenzene.....	3.0208 grams.
Chlorbenzene .....	6.3470 "
Calorimeter correction in weight of mercury.....	—0.0013 "
Weight of mercury moved .....	—0.0030 "
" " " " due to mixing of liquids.....	—0.0017 "
Thermal effect measured in lesser calories.....	—0.101 "

An inspection of the above data shows that none of the heat effects is much above the limit of accuracy of which the method was judged capable. It was deemed worth while, however, to make some determinations of the heat effects brought about by



mixing liquids by means of thermometric measurements, especially for mixtures of benzene and other liquids, as benzene in the pure state could not be used in the ice-calorimeter. The apparatus used, although simple, is capable of telling with considerable accuracy whether there occurs a change in temperature when two liquids are mixed. It consisted of a large U tube, in one branch of which was fitted a thermometer graduated in hundredths of a degree, such as described by Beckmann,<sup>1</sup> and recommended for cryoscopic and ebullioscopic work, and in the other a pipette similar to the one described above in connection with the ice-calorimeter. The U tube had a very narrow side tube towards the top of one branch, which when stopped with cotton wool permitted the egress of air without any evaporation of the liquids in the large tube to speak of. The stirrer employed was similar to the one used with the pipette in the ice-calorimeter.

A weighed quantity of one liquid was put into the U tube, and a quantity of the other liquid was weighed in the pipette. The thermometer and pipette were put in the tube tightly by means of good corks, the whole apparatus supported on a retort stand, and wrapped snugly with a thick layer of cotton wool. The apparatus was then set in a room the temperature of which could be easily kept within twenty-five to thirty degrees C. for several hours. By working at this rather high temperature, the disturbing effect due to the proximity of the person of the operator was considerably lessened. When the apparatus had remained in the room for a couple of hours, the thermometer was read off at intervals of a minute for ten minutes, the contents of the pipette made to flow into the U tube, the two liquids were mixed as rapidly as possible by a twirling and up and down motion of the pipette, around which was clasped the aluminum stirrer, and then the temperature was read off at each minute for ten minutes longer. The pipette was then again weighed so as to get the actual amount of the liquid discharged by it, since it never occurred that it emptied itself completely.

The experiments carried out by means of this thermochemical apparatus limit themselves to mixtures of benzene with monochlorobenzene and with chloroform. They, together with those

<sup>1</sup> *Ztschr. phys. Chem.*, 2, 644, 1888.

carried out with the ice-calorimeter, are perhaps sufficient to serve as experimental corroboration of the theoretical relations between heat of solution and vapor-tension.

It is perhaps best to append the whole series of determinations in order that the reader may judge for himself of the accuracy of the results.

CHANGE OF TEMPERATURE ON MIXING FOUR GRAMS MONOCHLORBENZENE AND 26.524 GRAMS BENZENE.

Before mixing.		After mixing.	
Minutes.	Thermometer readings.	Minutes.	Thermometer readings.
1	2.242°	11	2.339°
2	2.258°	12	2.348°
3	2.272°	13	2.369°
4	2.291°	14	2.381°
5	2.307°	15	2.388°
6	2.318°	16	2.390°
7	2.330°	17	2.396°
8	2.344°	18	2.394°
9	2.352°	19	2.388°
10	2.365°	20	2.380°

CHANGE OF TEMPERATURE ON MIXING 6.55 GRAMS MONOCHLORBENZENE AND 17.54 GRAMS BENZENE.

Before mixing.		After mixing.	
Minutes.	Thermometer readings.	Minutes.	Thermometer readings.
1	2.591°	11	2.709°
2	2.603°	12	2.751°
3	2.618°	13	2.803°
4	2.622°	14	2.820°
5	2.630°	15	2.829°
6	2.638°	16	2.838°
7	2.641°	17	2.847°
8	2.649°	18	2.853°
9	2.651°	19	2.861°
10	2.655°	20	2.872°

CHANGE OF TEMPERATURE ON MIXING 10.86 GRAMS MONOCHLORBENZENE AND 7.31 GRAMS BENZENE.

Before mixing.		After mixing.	
Minutes.	Thermometer readings.	Minutes.	Thermometer readings.
1	1.830°	11	1.421°
2	1.803°	12	1.400°
3	1.790°	13	1.395°
4	1.775°	14	1.372°
5	1.762°	15	1.370°
6	1.760°	16	1.420°
7	1.761°	17	1.435°
8	1.733°	18	1.450°
9	1.710°	19	1.445°
10	1.691°	20	1.438°

CHANGE OF TEMPERATURE ON MIXING 12.81 GRAMS CHLOROFORM AND  
11.87 GRAMS BENZENE.

Before mixing.		After mixing.	
Minutes.	Thermometer readings.	Minutes.	Thermometer readings.
1	1.489°	11	3.316°
2	1.520°	12	3.348°
3	1.531°	13	3.321°
4	1.540°	14	3.280°
5	1.561°	15	3.262°
6	1.573°	16	3.236°
7	1.582°	17	3.186°
8	1.608°	18	3.160°
9	1.621°	19	3.138°
10	1.632°	20	3.132°

It is apparent from these results that the change of temperature when benzene and monochlorobenzene are mixed does not exceed but a few hundredths of a degree, and even when the relative amounts of the liquids are about the same the change is in one case positive, in another negative, so that it is perhaps legitimate to judge that the change of temperature is largely due to the probability that the two liquids are at slightly different temperatures to begin with, and that in reality no or but an exceedingly slight heat effect occurs when these two liquids are mixed.

In the mixing of benzene and chloroform, however, there is a considerable rise of temperature, as indeed might be expected, since mixtures of chloroform and benzene do not in their vapor-tensions present the simplest phenomena. I have experimented with several other mixtures of liquids not belonging to the first class, especially with the ice-calorimetric method, and have found that they present certain abnormalities, some absorbing heat, and some evolving heat; these determinations, together with certain theoretical considerations, will form the substance of a subsequent paper.

Considering the above experiments as a whole, we may conclude that they are in entire corroboration of the formulas (A), (B), (C), and (D).

Nernst<sup>1</sup> found by the comparison of the theoretical conclusions with certain experimental data that the maximum of work, ob-

<sup>1</sup> Ueber die mit der Vermischung Konzentrierter Lösungen verbundene Aenderung der freien Energie: Sonderabdruck aus Nr. 12 der Nachrichten von der Königl. Gesellschaft der Wissenschaften zu Göttingen. v. J., 1892.

tainable by mixing two concentrated solutions with the same solvent, is "often" equal to the concurrent thermal change.

He then proposes to call "a homogeneous mixture of two substances, of which the maximum of work which can be obtained by a change of its composition, is measured by the concomitant thermal phenomena," an "ideal concentrated solution."

The contrast between "ideal dilute solutions" and "ideal concentrated solutions" is best shown by a consideration of the equation which rules over all Nature's happenings; this, according to Helmholtz,<sup>1</sup> is

$$F - Q = T \frac{\delta F}{\delta T}$$

wherein  $F$  represents the decrease in the "free energy" (*freie Energie*);  $Q$  that of the "total energy" (*Gesamtenergie*), and  $T$  the initial and final temperature, assumed to be the same in the operation under consideration. The characteristic of the "ideal dilute solutions" is that  $Q = 0$  and that of the "ideal concentrated solutions" is that  $F = Q$ .

My object in mentioning these acute distinctions by Nernst is to call attention to the fact that there are certain combinations of substances (liquids) which, when mixed, develop no or very little heat, no matter what the relative proportions may be; that is, there exist "ideal dilute solutions" which may have any composition whatsoever, or, in other words, concentrated solutions may often follow the laws supposed to belong exclusively to dilute solutions. It is questionable, then, whether the notion of "ideal concentrated solutions" is necessary in science.

#### 15. VAPOR-TENSIONS OF MIXTURES OF ACETIC ACID WITH BENZENE AND WITH TOLUENE.

Two series of determinations were carried out on the mixtures of benzene and acetic acid, one at 35° and one at 20°, but one, however, for the mixtures of toluene and acetic acid, at 35°. In order to apply to the experimental results of the work, our mode of calculation of the vapor-tensions, it is necessary to know the molecular mass of gaseous acetic acid at the above two temperatures. Now acetic acid even in the vaporous condition is

<sup>1</sup> Zur Thermodynamik chemischer Vorgänge. Sitzungs-Berichte der Berliner Akademie, 22, 1882.

made up in part of polymerized molecules, so that it is not legitimate to set its molecular mass equal to that corresponding to the formula  $C_2H_4O_2$ . What the actual molecular mass of the gaseous acid at  $35^\circ$  and  $20^\circ$  is, can be easily calculated by the aid of the vapor-density determinations of Bineau<sup>1</sup> which are the more applicable to the case in hand as his vapor-density measurements were made under the same conditions as my vapor-tension determinations; that is to say, Bineau measured the amount of acetic acid that diffused into a definite volume of air at a fixed temperature. The molecular mass of acetic acid as deduced from Bineau's observations, is 104 for  $35^\circ$  and 110 for  $20^\circ$ . It may be worth while to remark that an error of five in the molecular mass will not entail an error of one millimeter in the vapor-tension: we may with all confidence then adopt the above molecular masses of acetic acid in state of vapor as quite accurate.

The necessary data of the experiments are given in tables XI to XIII, the superscription to each vertical column renders any explanation of them here superfluous.

TABLE XI.

*Vapor-Tensions of Mixtures of Benzene and Acetic Acid at  $35^\circ$ .*

*Vapor-Tension of Benzene at  $35^\circ$  is 146 mm. of Mercury.*

*Vapor-Tension of Acetic Acid at  $35^\circ$  is 26.5 mm. of Mercury.*

Per cent. of $C_2H_4O_2$ in liquid mixture.	Per cent of $C_2H_4O_2$ in gaseous mixture.	Grams $C_2H_4O_2$ in va- por.	Grams $C_2H_4O_2$ in va- por.	Tension of $C_2H_4O_2$ in mm.	Tension of $C_2H_4O_2$ in mm.	Volume of air in mm.	Barom- eter in mm.	Inter- nal pressure in mm.
6.44	2.45	0.0461	1.3759	3.5	140.0	1955	758	14
15.17	4.74	0.0834	1.3580	6.4	129.2	1958	758	15
37.10	8.25	0.0700	1.5840	10.5	117.0	1020	767	16
43.99	11.02	0.0867	0.5243	13.2	106.5	1019	766	16
49.86	12.26	0.0931	0.4849	14.0	103.1	1020	766	17
53.24	13.33	0.0969	0.4731	14.9	97.6	1020	766	17
54.65	13.82	0.0990	0.4630	15.3	97.3	1020	766	17
56.60	14.62	0.1063	0.4677	16.4	96.0	1020	766	17
73.87	20.18	0.1156	0.4585	18.4	72.7	1019	766	16
80.00	26.91	0.1351	0.2751	22.3	59.3	1020	766	17

TABLE XII.

*Vapor-Tensions of Mixtures of Benzene and Acetic Acid at  $20^\circ$ .*

*Vapor-Tension of Benzene at  $20^\circ$  is 75.6 mm. of Mercury.*

*Vapor-Tension of Acetic Acid at  $20^\circ$  is 11.7 mm. of Mercury.*

<sup>1</sup> Recherches sur les Relations des Densités des Vapeur avec les Équivalent Chimiques: *Ann. chim. phys.*, 18, 226, 1846.

Per cent. of $C_6H_4O_3$ in liquid mixture.	Per cent. of $C_6H_4O_3$ in gase- ous mixture.	Grams $C_6H_4O_3$ in va- por.	Grams $C_6H_4$ in va- por.	Tension of $C_6H_4O_3$ in mm.	Tension of $C_6H_4$ in mm.	Volume of air in cc.	Barom- eter in mm.	Inter- nal pressure in mm.
53.24	11.99	0.0440	0.2291	6.6	48.7	1018	760	16
80.00	21.97	0.0576	0.2100	9.1	33.0	1018	760	16
97.28	64.66	0.0674	0.0276	11.4	6.2	1018	760	16

TABLE XIII.

*Vapor-Tensions of Mixtures of Toluene and Acetic Acid at 35°.*

*Vapor-Tension of Toluene at 35° is 47.2 mm. of Mercury.*

*Vapor-Tension of Acetic Acid at 35° is 26.5 mm. of Mercury.*

Per cent. of $C_6H_4O_3$ in liquid mixture.	Per cent. of $C_6H_4O_3$ in gase- ous mixture.	Grams $C_6H_4O_3$ in va- por.	Grams $C_6H_4$ in va- por.	Tension of $C_6H_4O_3$ in mm.	Tension of $C_6H_4$ in mm.	Volume of air in cc.	Barom- eter in mm.	Inter- nal pressure in mm.
49.00	32.66	0.0911	0.1661	15.0	31.8	1020	760	18
60.88	37.91	0.1025	0.1485	17.4	28.5	1020	760	18
83.37	56.36	0.1252	0.0858	22.2	16.7	1020	760	18

From the above data curves were constructed on a large scale with percentages of composition as abscissas and vapor-tensions as ordinates (one inch on the axis of abscissas corresponded to five per cent.; one inch on axis of ordinates to ten mm. of pressure); these proved to be perfectly regular, and passed directly through most of the points.

The points for acetic acid either fell upon or very close to the straight line connecting the left hand origin of the coordinate system with the point on the right hand axis of ordinates corresponding to the value of the vapor-tension of pure acetic acid at the temperature in question, *viz.*; 26.5 for 35°, and 11.7 for 20°, the acetic acid vapor-tension curve is simply a straight line, then, when the composition is expressed in percentages. An interesting conclusion to be drawn from this fact is that the partial tension of acetic acid is the same, be it mixed with benzene or with toluene; the specific influence of the diluting liquid seems to be extremely slight; if, indeed, there is any at all. This circumstance also indicates that the molecular condition of the acid is the same when it is dissolved in either of the hydrocarbons so as to form solutions of the same strength; this insight into the molecular structure of acetic acid enables us to determine by a little calculation its molecular mass not only in the dissolved but also in the pure state. In the following section will be set forth the *modus operandi*.

From the curves drawn as just described above, the partial pressures of the various constituents of the mixtures were taken for concentrations corresponding to ten, twenty, thirty, ..... ninety per cent. of acetic acid; the data thus obtained are given in Table XIV.

TABLE XIV.

*Partial Pressures of Benzene, Acetic Acid, and Toluene.*

Per cent. of $C_2H_4O_2$ in liquid mixture.	Partial pressure of $C_2H_4$ at 35° in mm.	Partial pressure of $C_2H_4O_2$ at 35° in mm.	Partial pressure of $C_2H_6$ at 35° in mm.	Partial pressure of $C_6H_6$ at 20° in mm.	Partial pressure of $C_2H_4O_2$ at 20° in mm.
10	138.4	2.8	44.5	71.4	1.2
20	130.9	5.6	41.6	67.5	2.3
30	122.2	8.2	38.6	63.1	3.5
40	112.6	11.1	35.0	58.2	4.8
50	102.4	13.6	31.9	53.2	6.0
60	90.7	16.2	27.8	47.1	7.2
70	76.7	19.1	23.1	40.1	8.4
80	59.1	21.7	18.4	31.1	9.6
90	35.1	24.2	11.1	18.5	10.7

#### 16. THE MOLECULAR MASS OF LIQUID ACETIC ACID AND A GENERAL METHOD OF DETERMINING MOLECULAR MASSES OF LIQUIDS.

The data given in the preceding section on the vapor-tensions of mixtures of acetic acid and benzene, taken in connection with the fact that the partial tension of benzene in its solutions is directly proportional to its concentration, permit of determining the molecular mass of the acid when diluted to any degree whatsoever with the hydrocarbon; and this special case may be generalized so as to permit of universal application. Furthermore, if the molecular mass of a substance be known in solutions of every degree of concentration, it is possible by a little extrapolation to pass over to the molecular mass of the pure liquid. It is, of course, assumed in making such an extrapolation that no break occurs in the continuity of the phenomenon, that is, the addition of very small quantities of a normal liquid to an associated one occasions correspondingly small changes in the degree of complexity of the molecules of the latter.

The way in which I have gone about to get at the molecular mass of acetic acid in benzene and toluene solution is as follows:

In a system of coordinates, molecular masses of acetic acid from 0 to 100 were laid off on the axis of abscissas (twenty inches

long), and on the axis of ordinates, the vapor-tensions were taken from 0 to 150 mm. of mercury (fifteen inches long). A straight line was drawn from the point 100 on the axis of abscissas and 0 on the right-hand axis of ordinates to the point 0 on the axis of abscissas and 146 (benzene at  $35^\circ$ ), 75.6 (benzene at  $20^\circ$ ), and 47.2 (toluene at  $35^\circ$ ). Upon this straight line must lie all the points corresponding to the partial tensions of benzene or toluene dissolved in acetic acid. So points were marked along it giving the value of the partial tensions of benzene and toluene in solutions containing ten, twenty, thirty, etc., per cent. of acetic acid, the data being taken from table XIV.

The value of the abscissas which these points determine give the number of molecules of acetic acid contained in 100 molecules of the mixture. All that has to be done now is to solve for every case this problem: Given a mixture containing  $m$  parts of a liquid  $A$ , having a molecular mass  $z$ , and  $n$  parts of a liquid  $B$ , having a molecular mass  $y$ ; the mixture is made up of  $r$  molecules of  $A$ , and  $s$  molecules of  $B$ . What is the value of  $x$  in the terms of  $y$ ,  $m$ ,  $n$ ,  $r$ , and  $s$ ?

In the case before us, we will take acetic acid for the liquid  $A$ , and benzene, or toluene as the case may be, for  $B$ ; then  $n$  is equal to  $(100-m)$ , and  $s$  to  $(100-r)$ .

It is easily found that the solution of our problem is

$$x = \frac{m s y}{r n} \text{ or } x = \frac{m (100-r) y}{(100-m)r}.$$

In the accompanying tables, XV, XVI, and XVII, the values of  $m$ ,  $r$ , and  $x$ , are given.

TABLE XV.

*Molecular Mass of Acetic Acid dissolved in Benzene at  $35^\circ$ .*

Percent. $C_2H_4O_2$ in liquid mixture.	Molecules $C_2H_4O_2$ in 100 molecules of liquid mixture.	Molecular mass of acetic acid.
10	5.2	158
20	10.6	164
30	16.6	167
40	23.1	173
50	30.0	182
60	37.7	193
70	47.2	203
80	59.3	213
90	75.6	227
100	100.0	240



TABLE XVI.

*Molecular Mass of Acetic Acid dissolved in Benzene at 20°*

10	5.1	161
20	10.5	166
30	16.2	172
40	22.6	177
50	29.6	186
60	37.2	198
70	46.7	208
80	58.7	218
90	75.2	231
100	100.0	244

TABLE XVII.

*Molecular Mass of Acetic Acid dissolved in Toluene at 35°.*

Per cent. of $C_2H_4O_2$ in liquid mixture.	Molecules $C_2H_4O_2$ in 100 molecules of liquid mixture.	Molecular mass of acetic acid.
10	6.1	159
20	12.4	163
30	19.0	168
40	26.5	170
50	32.8	188
60	41.3	196
70	51.2	204
80	61.1	213
90	78.4	228
100	100.0	240

Considering tables XV and XVII first, we see that the values of  $x$  are approximately the same, the molecular mass of the acid becoming less and less as it is more and more diluted with benzene or toluene. It is remarkable that these two series of values for  $x$  fall out so nearly the same, for in the mixture of toluene and acetic acid, the differences of their vapor-tensions is so slight that the line of partial pressures of toluene is nearly horizontal, and an error of one millimeter in the determination of the partial pressure may occasion an error of four units in the molecular concentration; in the mixture of benzene and acid, however, the error arising from this source is not more than three-tenths of a unit, the angle made by the line of partial pressures being considerably greater than in the case of the other mixture.

For the determinations carried out at 20° on the mixture of benzene and acetic acid, it is seen that the number of molecules

of acid is less, and hence their molecular mass is greater, than when the determinations were carried out at  $35^{\circ}$ . This is just what is to be expected for the lowering of temperature has been found to be invariably accompanied by an increase in the condensation of the molecule.

I have sketched the curves corresponding to the values of  $m$  and  $x$  given in the foregoing tables, in a system of coordinates with percentage composition as axis of abscissas and molecular masses as axis of ordinates.

The curves for the mixture of acetic acid and benzene at  $35^{\circ}$  practically coincides with that of the mixture of acetic acid and toluene at  $35^{\circ}$ , while the curve for the mixture of benzene and acetic acid at  $20^{\circ}$  is parallel and slightly above the other two. The curves are perfectly regular in form, and if prolonged to cut the right-hand axis of ordinates cannot give values varying by more than one unit; accordingly it may be claimed that the point where the axis of ordinates is cut by the extrapolated curve gives to about one unit the molecular mass of acetic acid in the liquid state at the temperature taken for the determinations. The results of my extrapolations gives as the molecular mass of liquid acetic acid at  $35^{\circ}$ , 240, and, at  $20^{\circ}$ , 244.

It is interesting to compare these results with those obtained by Ramsay and Shields.<sup>1</sup> These investigators found by the determination of the superficial tension of acetic acid that its molecular mass between the temperature limits,  $16^{\circ}$  and  $46^{\circ}$ , was equal to 217.2 ( $60 \times 3.62$ ); although this result leaves room for considerable uncertainty as to what the molecular mass of the acid is at any given temperature between these limits, it is in corroboration of my results; for, as has been well established, the degree of association in the molecules of a complex liquid is greater the lower the temperature, and my results pertain to temperatures which are lower or about the same as the mean of the two extreme temperatures given by the two English chemists.

The method of determining the molecular masses of liquids described in this section is the only one as yet devised, which permits of the determination at any given temperature of the mass of the molecule.

<sup>1</sup> Ueber die Molekulargewichte der Flüssigkeiten. *Ztschr. phys. Chem.*, 12, 470, 1893.

It is founded on empirical results and depends upon no hypothesis other than the universally recognized one of Avogadro. It is applicable to all cases where the substances under examination can be accurately analyzed. It calls for no special apparatus, even a modest laboratory being provided with the necessary pieces. It requires no great amount of manipulative skill, and the results are obtained in relatively short time. I hope that it will be rigidly tested by chemists, and any omissions of this mere sketch be supplied.

#### RESUMÉ.

The main results of this article may be summed up as follows :

1. A method of determining the partial pressures of mixtures of liquids has been elaborated, and its sources of error discussed.
2. Although the method can be said to give the vapor-tensions of pure liquids with an accuracy equal to that obtainable by the best of other methods only when the liquids are not very volatile, the results obtained by it for mixtures of liquids of not too different volatilities are accurate enough to serve as the experimental basis for theoretical deductions and generalizations.
3. A number of mixtures of representative liquids have been investigated as regards their vapor-tensions.
4. In some cases, extremely simple relations were found ; in others, certain complexities presented themselves.
5. A recalculation of Regnault's determinations of the vapor-tensions of some mixtures of normal liquids as well as a consideration of Raoult's conclusions and Brown's work on the boiling-points of solution showed that it was permissible to apply what was found true for any one temperature to any other.
6. The relations between the concentrations in the gaseous and liquid phases were found to be quite simple and entirely in accordance with the provisions of the theoretical relations established by Planck and Nernst.
7. The changes of temperature occurring when certain liquids were mixed were found to be very small, and the resulting mixtures were those which exhibited the simplest relations in their vapor-tensions.
8. The vapor-tensions of mixtures of acetic acid with benzene and with toluene were determined, and the results were such as

to permit of the determination of the molecular mass of the dissolved and liquid acid.

9. A general method for the determination of the molecular masses of associated liquids at any given temperature was developed and illustrated with acetic acid.

The experimental part of this investigation was done in a laboratory in the School of Mines at Paris, placed at my disposition by the authorities of that noble institution; and I here take the pleasant privilege of thanking them for the courtesy thus extended to me. My cordial thanks are also due to M. Emilio Dammour, *Ingénieur civil des Mines*, for his foreseeing kindness in furnishing me with apparatus and material; especially are my thanks due, however, to M. H. LeChatelier, *Ingénieur en chef des Mines*, whose wise direction and good counsel have been of great value to me throughout the work.

CHICAGO, May 1, 1895.

### WARNING AGAINST THE USE OF FLUORIFEROUS HYDROGEN PEROXIDE IN ESTIMATING TITANIUM.

BY W. F. HILLEBRAND.

Received May 29, 1895.

DUNNINGTON<sup>1</sup> has pointed out a source of error to be guarded against in estimating titanium in rocks and minerals by Weller's method, due, as he believes, to the partial reversion, in certain cases, of ordinary titanite to meta-titanite, which does not afford a yellow color with hydrogen peroxide. It remains for me to indicate another source of error in the possible presence of fluorine in the hydrogen peroxide.

For two years the colorimetric method has given reasonable satisfaction in this laboratory, but recently a new lot of hydrogen peroxide was purchased of a different brand from that hitherto used, and, after a time, it was noticed that the results obtained were in some instances far too high, and that no two determinations agreed.

It is known that hydrogen peroxide does not produce a yellow color in titanium solutions carrying hydrofluoric acid or fluorides, and moreover the addition of even a drop of the dilute acid to

<sup>1</sup> This Journal, 13, 210.

an already peroxidized titanium solution weakens the color. For this reason it is necessary to take the greatest care to insure the complete expulsion of all fluorine when dissolving rocks or minerals by means of hydrofluoric and sulphuric acids prior to the colorimetric estimation. A drop of hydrofluosilicic acid acts similarly, but the latter reagent cannot be made to completely discharge the color even if added in great excess.

This, however, was not suspected as the cause of our trouble until, on referring to the circular of one of the leading makers of hydrogen peroxide in this country, whose product has always given satisfactory results in titanium work, it was found that among the various acids enumerated as usually to be found in the commercial article, hydrofluoric acid appears. Talbot and Moody, in the *Technology Quarterly*, 5, 123, mention hydrofluosilicic acid as of frequent occurrence in the peroxide manufactured a few years ago. On examining the suspected peroxide by neutralizing with fixed alkali, evaporating to dryness, and heating with strong sulphuric acid, fluorine was detected by the odor of the acid evolved and by its action on glass.

It is therefore imperative to use only hydrogen peroxide which is free from fluorine in estimating titanium, for its presence may utterly vitiate the results, even if only two or three cc. of the peroxide are employed.

LABORATORY OF THE U. S. GEOLOGICAL  
SURVEY, WASHINGTON, D. C.

---

[FROM THE CHEMICAL LABORATORY OF THE LANDWIRTSCHAFTLICHEN-  
LANDES-LEHRANSTALDT IN CZERNOWITZ.]

## THE VISCOSIMETRIC EXAMINATION OF BUTTER FOR FOREIGN FATS.

BY DR. NEWMANN WENDER.

Received July 1, 1895.

**T**HROUGH a large number of investigations by Poisenille,<sup>1</sup> Girard, Hagenbach,<sup>2</sup> Graham, Rellstab, Pribram and Handl, Traube and Gartenmeister, to whose original investigations the reader is referred for the sake of brevity, it has been

<sup>1</sup> *Ann. der Phys. u. Chem. Pogg.*, 58, 424. *Ann. chim. phys.*, 64, 129.

<sup>2</sup> *Ibid.*, 99, 217.

established that a relation exists between the chemical composition of liquids and the velocity of transpiration just as there exists a relation between boiling-point and composition. There exists now a criterion for the purity of a substance, if a relation is found to exist between viscosity and boiling-point, at the same time, points of practical importance. From the investigations of Pribram and Handl it follows that observations of the specific viscosity or specific transmissibility of substances afford a hint as to the presence of adulterations and impurities, because these exert a decided influence upon the fluidity. The determination of the viscosity has found a practical value in the examination of oils and beer. The apparatus used for this purpose have been the viscometer of Engler and the septometer, both of which have found extended application. To these valuable, yet always expensive forms of apparatus, I have recently added the "Fluidometer," devised by me and manufactured by the firm of Max Kaehler and Martini, Berlin. I have communicated a description of the same to the Pharmaceutical Society of Berlin.<sup>1</sup> The apparatus possesses besides its inexpensiveness, other merits, chief among which is this, that by means of a simple compression bulb the liquid can be forced back and used for repeated determinations. The apparatus consists of a U formed capillary tube, both of whose limbs are enlarged and divided in such a manner that one arm holds ten cc. and the other two cc. liquid. According to the laws of communicating tubes the liquid flows from the wide limb through the capillary into the smaller limb, which is placed somewhat lower. The viscosity is calculated from the time which is required for the liquid to flow from the first division to the last upper division. There is no danger of error arising from evaporation or contamination with foreign substances in repeating the experiments, and, furthermore, the apparatus is easily and quickly cleaned.

According to the researches of Graham, in 1861,<sup>2</sup> confirmed by those of Pribram and Handl,<sup>3</sup> and by those of Gartenmeister,<sup>4</sup> it was found that the viscosity of a liquid increased with

<sup>1</sup> *Ber. d. Phys. Ges.*, Berlin, 1891, 342.

<sup>2</sup> *Ann. Chem.* (Liebig), 123, 90.

<sup>3</sup> *Loc. cit.*

<sup>4</sup> *Ztschr. phys. chem.*, 6, 524.

the molecular weight, and the correctness of this law is evident from the following table :

Fatty acids.	Molecular weight.	Pribram and Handl.					Gartenmeister.
		Specific gravity at 20° C.	Boiling-point.	Specific viscosity at 10° C.	Specific viscosity at 30° C.	Specific viscosity at 50° C.	
Propionic acid.....	74	0.9929	140.7	70.3	51.5	49.9	—0.1128
Butyric acid .....	88	0.9580	163.0	110.2	77.4	57.6	—0.1634
Valerianic acid.....	102	0.9386	184.0	152.4	103.3	71.5	—0.2279
Capronic acid.....	116	0.9279	199.7	222.2	139.7	97.8	—0.3263
Heptylic acid .....	130	0.9163	223.0	....	....	....	—0.4440
Octylic acid.....	144	0.9115	237.0	....	....	....	—0.5860
Nonylic acid.....	158	0.9053	253.0	....	....	....	—0.8480

Butter-fat differs from other animal fats in that it contains besides the glycerides of the higher fatty acids, a large amount of the glycerides of butyric, capronic, caprylic, and caprinic acids, and according to the investigations of Duclaux<sup>1</sup> the probable mean composition of butter-fat is :

Palmitin, stearin, olein, } .....	91.5 per cent.
Traces of myristin butin }	
Butyrin .....	4.2 "
Capronin .....	2.5 "
Caprylin, caprinin, laurin (traces).....	1.8 "

100.0

It appears therefore that mangarin consists of the glycerides of palmitic, stearic, and oleic acids only. If we compare the molecular weights of the constituents, it follows that the molecular weights of the glycerides of the higher fatty acids are much higher (806–890) than those of the glycerides in natural butter (302–470). The molecular weight determinations of Gaselli and Carcano<sup>2</sup> showed that the molecular weight of pure butter lies between 696–715 while that of margarin lies between 780–883. The fact that molecular weight stands in close relationship with viscosity was confirmed by Killing,<sup>3</sup> although it is known that

<sup>1</sup> Fleischman, *Lehrbuch der Milchwirtschaft*, Bremen, 1893, 30.

<sup>2</sup> Centrbl. Agr. Chem., 1894, 838.

<sup>3</sup> *Ztschr. Angew. Chem.*, 1894, 643.

different samples of margarin show variable values, which could appreciably influence the results in the calculations.

Since it has been demonstrated by the work of Traube<sup>1</sup> that the relation between molecular weight and viscosity is not affected by solvents, I used in my "Fluidometer" a solution of the melted fat in chloroform, merely to avoid the difficult operation of maintaining the melting-point temperature of the fat and I did not lose sight of the fact that the viscosity of the solvent had to be taken into account. Chloroform was used, samples of which from different sources, required, in the mean, 20.04 seconds at 20° C. for efflux. The time of transmission of the solvent is set at 100 and the calculations for solutions are based upon this. From a large number of results I present the following average :

Viscosity value for pure butter	344.30	Time, 68.8
" " " margarin	373.20	" 77.4

Killings' investigations show further that with the one exception of cacao-fat, whose viscosity value falls below that of pure butter-fat, the values for vegetable fats, used by margarin manufacturers are decidedly higher.

Since, however, mixtures can be made whose values approximate that of butter-fat, the Reichert-Meissl method must be resorted to in order to detect the fraud.

A longer or shorter period of standing of the fat solution does not influence the result, whereas every degree of temperature above 20° C. decreases the time of efflux by 1.45 seconds. On the other hand, a decreasing temperature naturally has a retarding influence which averages 1.43 seconds for every degree. The determination of the exact amount of margarin added to butter when the amount of the former is small, cannot be expected of this method, but a largely adulterated sample is easily detected. From the above the following conclusions may be drawn :

1. The viscosity of butter-fat, in chloroform solution, as well as in the pure state, is always decidedly smaller than that of margarin or its solution of equal amount.
2. While the viscosities of different samples of butter show

<sup>1</sup> Berliner, Ber., 1886, 871.



relatively small differences, samples of margarin from various sources, show much larger differences.

3. The viscosimetric determination can yield as good service in distinguishing butter-fat from margarin as any other physical method. The amount of margarin added to butter may also be approximately determined.

4. On account of its easy manipulation, its inexpensiveness, and the small amount of fat necessary, the "Fluidometer" is capable of yielding excellent results, not alone in the hands of experienced chemists, but likewise in those of government inspectors, etc.

## THE EXAMINATION OF LARD FOR IMPURITIES.

BY DAVID WESSON.

Received June 22, 1895.

IN examining a sample of any material for impurities the analyst must first familiarize himself with the pure substance before he can detect wherein the sample under examination differs. If a definite compound is being dealt with, the problem is an easy one, but if we have an organic substance, which from the very nature of its origin is subject to many variations, the analyst is confronted with a problem of no small magnitude, and this is very true in regard to the accurate analysis of commercial lard, which is the fat rendered from various parts of the freshly slaughtered swine. Hogs being omniverous animals, it is reasonable to suppose that the fat will vary in accordance with the feed. It is a well-known fact that the lard from hogs which have been allowed to run in the woods and fatten on nuts of various sorts, preserves in a marked degree certain properties of the nut oils, and is much softer, containing more oil than that made from corn-fed hogs. That animals under proper conditions absorb food directly and deposit the same more or less unaltered in their tissues, seems to have been proven by experiments made some years ago at the Munich Physiological Institute.

That the fat varies greatly in different parts of the same animal has been demonstrated by various observers<sup>1</sup> as well as the writer.

<sup>1</sup> Wiley: Bulletin 13, Part IV, U. S. Dept. of Agr.; R. T. Thomson and H. Ballantyne; *J. Soc. Chem. Ind.* 9, 589, (590).

E. Spaeth<sup>1</sup> gives table of analytical data showing variations between back, kidney, and intestinal fat, taken from eight different hogs, of different ages. His results show considerable difference between the different animals.

The modes of rendering make considerable differences in the character of the fat. The comparatively low temperature used in kettle-rendering produces a fat of quite different analytical nature from that produced by treatment under high steam pressure in a closed rendering tank (*autoclave*). As most American lard is prepared by this latter method, this fact must be well borne in mind in interpreting analytical results.

Time is an important factor in determining the condition of a lard. A lard several months old will give analytical data which if compared with those of a fresh sample, would indicate adulteration.

The lard analyst who knows nothing of the history of a sample, and without such experience as will enable him to judge by the senses what sort of lard he is dealing with, is extremely liable to misinterpret analytical results and fall into grievous errors.

The methods used for the detection of cottonseed-oil in lard depend upon specific color reaction with different reagents, different physical properties of the fats, and the differences between the fluid portion ("olein") of the lard and that of the cotton oil.

Considering these tests in their order, we will first consider the reaction with silver nitrate, commonly known as the "*Bechi Test*."

Cottonseed-oil when treated with an alcoholic solution of silver nitrate reduces the salt with formation of a brick-red or deep green color and deposition of metallic silver, while pure lard under like conditions should give little or no coloration and no metallic silver. The test has been applied in various ways by different chemists, but the writer has obtained the most satisfactory results by operating according to direction laid down by Dr. C. B. Dudley, in the Penn. R. R. specification for lard oil about six years ago. The solution used is made up with two grams silver nitrate, 200 cc. alcohol, and forty cc. ether. After expo-

<sup>1</sup> *Ztschr. Angew. Chem.* 1893, 133-136; also abstract in *Journal of the Society of Chemical Industry*, 12, 608.

sure to sunlight, till reaction ceases, the solution is decanted or filtered into a dark bottle.

In testing, ten grams of melted lard and five cc. of the solution are well stirred together on the water-bath at 100° C. for fifteen minutes, at the end of which time most of the alcohol will have passed off. With pure lard there should be no coloration, while in the presence of cottonseed-oil the depth of color varies according to the amount and character of the oil, and a metallic mirror is deposited on the surface of the liquid fat.

Applying the test, in the manner described, to samples of steam lard known to be pure, and representing many thousand tierces, the writer found that more or less coloration of a purple tint was the rule rather than the exception. Believing that this apparent reduction was due to organic matter of a reducing nature held in the lard as a result of the process of rendering, the experiment was tried of washing the lard with a two per cent. solution of nitric acid. For this purpose about fifty grams of melted lard in a flask are shaken up with twenty-five cc. of the diluted acid, and after allowing to settle on the water- or steam-bath, the acid water is removed and the lard washed once with fifty cc. of hot distilled water. After settling till clear, ten cc. of the lard are pipetted off and the test made as described. In nineteen cases out of twenty, pure steam lard after this treatment will give no reduction whatever or suspicion of reduction, the fat remaining colorless at the end of fifteen minutes, whereas the reducing matter of cotton oil being unaffected by this treatment would give an unmasked reaction with the silver nitrate. While in the majority of cases the above treatment is all that is necessary to remove accidental reducing matters, we occasionally meet lards which have been treated at very high temperature and for a long time, which show as a result a slightly higher than normal per cent of free acid (normal is four-tenths to one per cent) and contain decomposition products of the animal fiber which have a very strong reducing action on our silver solution. Such samples must be first washed with diluted caustic soda solution and distilled water, and afterward with the nitric acid, before any definite conclusion can be drawn from the results of applying the silver nitrate test.

The condemnation of a sample of lard which gives a coloration with silver nitrate, without first purifying the fat as indicated, would be as absurd as it would be unjust, yet many good analysts have been known to do this very thing.

Dr. Ernest Millau applies the silver nitrate to the freshly separated fatty acids, but insists most forcibly on a preliminary preparation of the fat for analysis by a purification somewhat similar to the one outlined above. (See pamphlet<sup>1</sup> published by Ministère de L'Agriculture.)

Exception is taken to the silver nitrate test by various writers because of the misleading reaction obtained with lard improperly prepared for analysis, and also because cotton oil can be refined with oxidizing agents and the use of very high temperatures in such a measure as to destroy the specific reducing agent. Also very old oil will sometimes refuse to give any reduction. If such an oil were mixed with lard, it goes without saying that no reduction would not necessarily indicate pure lard, but the writer can say, as a result of several years' experience, that he has never run across any sample of oil failing to give the reaction which would be suitable to use in the preparation of an edible fat. If a lard containing cotton oil should become so old that the oil should lose its reducing power, the lard would be fit only for the soap-kettle.

The preponderance of evidence seems to be in favor of the silver nitrate test as being the best single test which has yet been brought forward for the detection of cotton oil in lard. When properly applied it is the most reliable for detecting small quantities.

The phosphomolybdic acid test, otherwise known as the Welmans test, first described in the *Pharm. Zeit.*, 1891, 36, 798, has been highly recommended by several writers, of late, as of value for the detection of vegetable oils in lard. Among them may be mentioned Rupp, Wimmer, Mansfield, and Goske, while H. Schweitzer and E. Lungwitz<sup>2</sup> state that they have found the test one of great value.

<sup>1</sup> Analyse Chimique des Matières Grasses Agricoles, par Ernest Millau, Directeur de Laboratoire d'Essais Technique de Marseilles.

<sup>2</sup> *J. Soc. Chem. Ind.*, 614, June 1894.

J. Lewkowitsch<sup>1</sup> says as the results of a series of careful experiments: "Welman's reaction can therefore be admitted as a preliminary test, the indications of which may, in some cases, give valuable hints as to the direction in which the examination of a sample has to be carried out and may serve as a useful corroboration of results obtained by other methods."

Samelson<sup>2</sup> concludes that the test is of no value and that the iodine figure is the only reliable test for the detection of cottonseed oil in lard. He bases the assumption on the fact that he found six samples of American lard with iodine numbers of 64.7 to 67.2, which were higher than any he had ever found recorded, whence he concluded that cotton oil must be present though not shown by the test.

George F. Tennille<sup>3</sup> publishes a very exhaustive paper on this test, and concludes that "the phosphomolybdic test may be considered to be of slight analytical value, and certainly does not fill that long-felt want of a simple test which will reliably indicate small percentages of cotton seed or other vegetable oils in lards." The writer has tried the test and arrived at the same conclusions.

*Sulphuric Acid Test.*—The color produced by the action of sulphuric acid on cottonseed-oil in a mixture with lard is often a good qualitative indication, but it so frequently happens that pure lards prepared under certain conditions will give similar coloration, that results must be taken with extreme caution, and in many cases had better not be taken at all.

Dr. J. Lewkowitsch<sup>4</sup> concludes: "The sulphuric acid color test may therefore only be used for purposes of preliminary information, and even then its indications should be interpreted with the greatest caution."

#### PHYSICAL TESTS.

*Specific Gravity.*—Lard freshly rendered in the writer's laboratory showed at  $\frac{99}{15}$ ° C. a specific gravity of 0.8600 to 0.8610, while old samples of known purity have been observed running as high as 0.8620, while we have on record one specimen which

<sup>1</sup> *J. Soc. Chem. Ind.*, 617, June 1894.

<sup>2</sup> *Ztschr. anal. Chem.*, 189, 1894.

<sup>3</sup> This Journal, 17, 33.

<sup>4</sup> Contributions to the Analysis of Fats, IV, Color Reaction, *J. Soc. Chem. Ind.*, 617, June, 1894.

ran as high as 0.8640, and gave no indication of cotton oil by other tests. The lard was nearly a year old and had been stored in tierces. Cottonseed-oil shows under like conditions 0.8683. With fresh lard as a standard we would have a difference between lard and cotton oil of 0.0083. The lard cited would therefore show  $\frac{0.0040}{0.0083}$  or forty-eight per cent. of cotton oil, which shows the test to give preposterous results when working on old lards. It is of use in obtaining the proportionate components of a mixture when the specific gravities of the identical fats used in preparing the mixture are known.

*Refraction Index.*—As this depends to a great extent on the relative amounts of olein and stearin and palmitin present, it is quite evident that two samples of lard containing these ingredients in different proportions would show different indices. Wiley has published a large number of refraction indices in Part IV, Bulletin 13, Dept. of Agriculture, 1889, Lard and its adulterations. In table 18, he gives the results of analysis of six samples of Prime Steam lard drawn by C. H. Mixer, the official inspector of the board of trade in Chicago, and accompanied by his affidavit. The lards were of unquestioned purity yet their indices varied from 1.4911 to 1.4675, which shows that the refraction index is little better than specific gravity as a test *per se*.

*Melting-point.*—Any one who has experimented much with the melting-points of lard and lard compounds will, it is believed, readily agree that no suitable method has yet been proposed which will give analytical indications of any value except in cases of large admixtures of beef fat. This determination depends so largely on the manner of cooling the fat and the time elapsing after the cooling that it is of no value whatever as an indication of small adulteration.

*Crystallizing-point of the Neutral Fat.*—The observation of the manner of crystallizing on cooling of the melted fat gives valuable indication regarding the presence of beef fat.

H. Schweitzer and E. Lungwitz,<sup>1</sup> give their mode of procedure and results obtained with it. They rely on the test to a

<sup>1</sup> Commercial Analysis of Lard, *J. Soc. Chem. Ind.*, June, 1894, 614, and July, 1894, 709.

considerable extent for the detection of beef fat. Amthor and Zink<sup>1</sup> use this method among others.

The writer has derived very useful indications respecting the proportion of beef fat present in a mixture, by working in a somewhat different manner. As a rule pure lards chill below 30° before showing turbidity, while if beef fat is present crystallization begins at higher temperatures according to the amount present. A lard containing ten per cent. of beef stearin will cloud at a higher temperature than pure lard stearin.

Microscopical examination of the fat crystals deposited from ether is of value for the identification of beef fat when present in large enough amount. When only small amounts of oleostearine are present the test is not as conclusive as the cooling test, unless recrystallization is resorted to.

*Crystallization-point of the Fatty Acids.*— This method, first proposed by Dalican, has for a long time been considered a valuable criterion and is a very useful factor in passing upon the purity of a lard.

The crystallization-point depends upon the relative amounts of solid and fluid acids present, being higher of course in proportion to the increase in the former, but unfortunately the thermometer readings are not in exact ratio to the amounts added.

As the relative amounts of the fluid and solid acids vary in different parts of the same animal it is quite evident that pure lards will show quite different points of crystallization, according to the portion of the animal from which they have been prepared, and also according to the individual, as shown by the results on lards rendered in the U. S. Agricultural Laboratory in Washington and in the writer's laboratory in Chicago some years since.

Part of hog.	According to	
	Wiley.	Wesson.
Head .....	36.6	35.4
Intestine .....	42.7	41.2
Leaf .....	41.3	41.5
Back and sides.....	...	39.7
Belly .....	...	39.7
Foot <sup>2</sup> .....	32.1	...

<sup>1</sup> *Ztschr. Anal. Chem.*, 1892, 584 to 537.

<sup>2</sup> This sample was prepared by a packer but well authenticated.

The crystallization-point of Prime Steam lard or the lard of commerce, varies from 35.5 to 38. The majority of receipts during the past year have shown an average to 36.5, which would indicate that more of the softer parts of the hog are now used than formerly, when the average was one degree higher.

Lard oil has a crystallization-point of  $31^{\circ}$ – $32^{\circ}$ , while well pressed lard stearin should show not less than  $43.5^{\circ}$ .

Considering the wide range in crystallization-point of pure lard, we can only regard the test as a corroborative one, and useful in connection with others in passing upon the purity of a lard, but of little value in proving presence of small amounts of either cotton oil or beef fat.

#### IODINE ABSORPTION.

As the amount of iodine absorbed by a fat depends upon the chemical nature and quantity of the fluid acids present it is evident that in the case of lards it is impossible to draw sharp conclusions, for the softer the lard the more iodine absorbed and conversely. If a standard for purity of lard should be established saying that the correct absorption should be a certain figure, there would be little trouble for the adulterator to make a mixture of cotton oil and beef fat which would fully meet the requirements, and thus make the iodine number prove nothing so far as purity of a lard is concerned. An example or two will make this apparent.

	Iodine number.		
Cotton oil.....	108	10 parts.	10.80
Oleostearin .....	21	10 "	2.10
Steam lard.....	64.5	80 "	51.80
Mixture has iodine number.....			64.50

and contains twenty per cent. of adulteration. The number 64.5 is very near the average for Prime Steam lard and well within limits. Another case would be that of a mixture of intestinal lard testing 52 and cottonseed-oil testing 108, which would contain twenty-five per cent. of the latter and still test 65, while with twenty per cent. cotton-oil the sample would have an absorption of but 63.

In our first example the Dalican temperature of crystallization would be raised a little above normal by the oleostearin, while



in the second instance it would be about normal for pure lard. By normal we mean the temperature of crystallization corresponding to the amount of fluid acid indicated by the iodine number.

Besides the variations caused by the fat being taken from different parts of the hog, we have the difference in individual animals, caused by difference in feed. For instance, Wiley,<sup>1</sup> found on testing the lard rendered in his laboratory from different parts of the same animal, figures which differ considerably from the writer's, as shown in the following table :

Portions of animal.	Wiley		Wesson.	
	Iodine No.	Point of crystallization.	Iodine No.	Point of crystallization.
Head.....	85.03	36.6	60.35	35.4
Intestine.....	57.34	42.7	52.14	41.2
Leaf.....	62.55	41.3	56.88	41.5
Back and sides...	. .	...	57.41	39.7
Belly.....	....	...	58.82	37.7

The results would seem to indicate that one of these hogs judged by the others must have been sadly adulterated. In the writer's opinion, the animal operated on by Wiley, which was purchased in Washington, was very likely one which had gathered a portion of its adipose in the woods of Virginia and adulterated its fat with the oils from beechnuts and acorns, while the writer's hog was a plain, every day Western corn-fed specimen, such as generally comes to the Chicago packers.

The crystallization-points would certainly indicate that considerable differences in the character of the oleins must be the cause of the great differences in the iodine numbers.

To observe the effects of age on samples, those of the writer cited above were tested again after three months standing in the laboratory at from 20° to 30° C., with the following results :

Head.....	63.64
Intestine.....	58.05
Leaf .....	61.02
Back and sides .....	60.50
Belly.....	63.95

Comparing these figures with those obtained on the fresh samples, which, if considered a standard of purity, would lead us to the conclusion that time had been adding some cotton oil. In

<sup>1</sup> Lard and Adulteration Bulletin 13, Pt. IV, U. S. Dept. of Agriculture.

the case of the leaf lard the quantity would appear to be eight per cent.

That age acts in a similar manner on steam rendered lard we can see no reason to doubt.

As a rule the iodine numbers of steam lards run considerably higher than most of the published results on lards.

The iodine numbers of prime steam lard range as follows :

Sample.	Crystallization-point.	Iodine number.	Remarks.
5662.....	39.30	61.95	Wiley: Lard and Adulterations; samples drawn and sworn to by C. H. Mixer, the official inspector at Chicago.
5663.....	38.05	63.82	
5664.....	....	60.34	
5665.....	....	65.12	
5666.....	39.10	60.85	
Sample.	Crystallization-point.	Iodine number.	Remarks.
1.....	36.3	67.22	Lard from 400 tierces and different packers.
2.....	36.0	65.25	
3.....	36.3	69.06	Age of samples, six to twelve months.
4.....	36.5	69.26	
5.....	35.6	67.30	All samples prime merchantable lard, and unquestionably pure. Tests made in our laboratory.
6.....	37.0	65.31	
7.....	37.3	64.31	
8.....	35.0	68.48	

L. E. Spaeth<sup>1</sup> gives results on fats from different parts of eight different hogs and draws the conclusion that a lard must not be considered adulterated merely because its iodine number surpasses sixty. Spaeth's results are :

Age of hog.	Iodine number of fat from		
	Back.	Kidney.	Intestines.
Two years.....	63.25	61.15	62.90
Six to eight months.....	62.95	49.35	57.25
Ten months.....	55.50	55.88	50.60
Six months.....	60.10	55.80	52.30
Five to six months.....	57.08	50.20	51.75
Six to seven months.....	63.61	52.35	49.85
Ten months.....	60.95	46.60	47.60
Six to seven months.....	61.20	51.50	52.85
Mean.....	60.58	52.60	53.10

The above results are especially instructive as showing the great difference which exists between different animals as well as different parts of the same animal.

<sup>1</sup> *Ztschr. Angew. Chem.* 1893, 133-136.

As commercial lard is nowadays made largely from heads, back, and side fat, it is easy to account for the high iodine absorption of prime steam lards.

#### IODINE NUMBER OF THE FLUID ACIDS.

As the fluid acids are the portion of the fat which absorb the iodine, and as the amount of fluid acids present in the fat determine its absorption, which also varies with the nature of the fluid acids present, it follows that the truly scientific method of analyzing a lard is to first determine the percentage of fluid acids present, and then from the iodine number of the fluid acids calculate the proportion of lard and cotton oil present.

This system of analysis was first published by Muter.<sup>1</sup> His process consists in precipitating the lead salts from a neutral solution, extracting the oleate with ether, decomposing the lead soap in the solution with dilute acid, determining the amount of oleic acid present by titrating a measured portion with standard alkali, and then determining the iodine number, using half a gram of the fluid acids under standard conditions. The process though tedious, gives very satisfactory results. Messrs. Muter and DeKoningh published some of the results of the process in the *Analyst*, Feb. 1890. They obtain for the fluid acids of tallow, 90; for lard, 93-94; while for cotton oil, 135.

N. J. Lane<sup>2</sup> reviews Dr. Muter's method, and describes an improvement which gives the results in much shorter time. His results, which were obtained in our laboratory, were as follows:

	Fluid Acids. Per cent.	Iodine number of same.	Hübl number of fat.	Saponifi- cation equiva- lent.	Crystalli- zation- point of fatty acids.
Cottonseed stearin .....	68.05	141.09	99.3	288.21	36.6
Summer yellow cotton oil	75.16	141.96	108.36	397.51	32.4
Winter yellow cotton oil..	77.64	143.49	110.96	296.27	30.4
Cotton oil, Columbia, S. C.	76.73	141.97	108.95	284.75	33.8
Cotton oil, New Orleans..	76.67	140.59	109.23	288.94	33.4
Steam lard, ave'ge sample	64.15	99.48	64.96	287.85	37.4
Corn oil (maize oil).....	83.97	144.40	121.7	.....	....
Arachide oil.....	79.84	114.00	93.55	.....	....

In studying the above table it will be noted in the case of cot-

<sup>1</sup> *Analyst* 1889.

<sup>2</sup> This JOURNAL, 15, 110.

ton oil, that whatever variation there may be in the other constants, the iodine number of the fluid acids shows comparatively little variation.

The sample of steam lard mentioned was a composite sample of a number of lots of known purity, representing the article as made at that time.

Wallenstein and Finck<sup>1</sup> work with a modification of the Muter method, which guards more fully against oxidation of the fluid acids by contact with air.

They say: "In deciding qualitatively as to the purity of a fat it may be assumed that below the limit of ninety-six (iodine number of fluid acids) there is no admixture of vegetable oil (except it be cocoanut oil, which is however revealed by the saponification number of the sample). *Between ninety-six and 105 much depends on the origin of the fat.* For instance, Central European lards show ninety-three to ninety-six, while American lards vary between 103 and 106, and additional confirmation by Welman's or Bechi's test will be required to form a decisive opinion."

Results obtained are as follows:

	Iodine number of fluid fatty acids.	Iodine number of Glycerides.
Berlin ox tallow .....	92.2	38.3
Australian tallow .....	92.4	45.2
Hungarian mutton tallow.....	92.7	38.6
American western steam lard.....	104.5	65.4
Berlin hogs' lard.....	96.6	52.7
Hungarian hogs' fat.....	96.2	60.4
Viennese hogs' fat .....	95.2	60.9
Roumanian hogs' fat.....	96.0	59.5
White American cottonseed-oil....	147.5	108.0
Yellow American cottonseed-oil... 147.3		107.8
Yellow Egyptian cottonseed-oil... 148.2		108.0
White English cottonseed-oil..... 146.8		106.5
White German cottonseed-oil ..... 147.1		107.1
Yellow Peruvian cottonseed-oil.... 147.8		106.8
Maize oil .....	140.7	122.0
Arachis oil.....	128.5	98.5

The above results agree fairly well with Lane's, and are another contribution to the variation of hog fats. The authors attribute the high iodine absorption of the American lard to the

<sup>1</sup> *Chem. Ztg.* 12, 1189-1191; also *J. Soc. Chem. Ind.* Jan. 31, 1895, 78.

difference in feeding methods pursued in America and Europe. They are no doubt right, though the mode of rendering also differs.

At the present time the writer is aware of no method of analysis approaching the modified method of Muter for accuracy, and invariably applies it in doubtful cases.

G. Halphen<sup>1</sup> gives results of a method of separating the fluid and solid fatty acids based on difference in solubility of zinc salts in carbon bisulphide. Their results show that very imperfect separations are obtained and the process has little practical utility. The writer tried the same method in 1888, using gasoline, and obtained better but not satisfactory results.

In conclusion, I would say that working with the best analytical methods at our command, unless the origin of samples is known, the analyst is frequently at a loss to interpret results, in much the same manner as in passing upon a potable water of unknown history, and often when we see the self-confident manner in which small percentages of cotton oil are announced on very questionable data, we feel like exclaiming with the poet,

"Fools rush in where angels fear to tread."

March 12, 1895.

---

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF  
CHEMISTRY. No. 7.]

## THE ACTION OF HALOID ACIDS IN GAS FORM UPON THE SALTS OF ELEMENTS OF GROUP V OF THE PERIODIC SYSTEM.

BY EDGAR F. SMITH AND FRED. L. MEYER.

Received May 3, 1895.

**A**FTER observing the conduct of salts of the acids of elements of Group V toward hydrochloric acid gas, it was but natural that we should, with some interest, note the results arising when the other haloid acids, in gas form, were substituted for hydrogen chloride. It was useless to predict what might occur, and, therefore, the slight variations from preconceived notions were in no wise surprising. Taking up the study of the haloid acids and the various salts in the order of increasing molecular magnitude, we began with

<sup>1</sup>*J. de Pharm. et Chim.*, 30, 241-247, 1894.

### 1. THE ACTION OF HYDROFLUORIC ACID GAS UPON SODIUM NITRATE.

The salt was exposed to the action of the gas in a platinum boat, carried in an iron tube. The temperature at which the reaction was conducted did not exceed  $250^{\circ}$  C. Not more than twenty minutes were allowed, or required, for the change which, from the analytical result given below, is evidently complete.

*Experiment.*—0.1052 gram of sodium nitrate gave 0.0530 gram of sodium fluoride, instead of 0.0520 gram, the theoretical amount.

A second trial gave a similar quantitative result.

### 2. THE ACTION OF HYDROFLUORIC ACID UPON PHOSPHATES.

The gaseous acid expelled nothing from sodium pyrophosphate. The boat contents sustained no less in weight. The water in the receiver gave no evidence of the presence of phosphorus when tested for it.

### 3. HYDROFLUORIC ACID AND VANADATES.

Sodium vanadate, thoroughly dried, was heated to  $250^{\circ}$  C., for one-half hour in an atmosphere of the acid vapor. Vanadium was found both in the receiver and in the boat. Upon repeating the experiment, increasing the temperature, and continuing the action of the acid vapor through an hour, about one-half of the vanadic acid was volatilized.

### 4. HYDROFLUORIC ACID AND ARSENATES.

In these trials sodium pyroarsenate was heated to about  $400^{\circ}$  C., while exposed to a brisk current of the acid vapors.

*Experiment 1.*—0.1893 gram of sodium pyroarsenate was used. When the boat-contents were examined 0.0872 gram of the pyro-salt was found unvolatilized.

*Experiment 2.*—0.2015 gram was treated in the same manner, with practically the same result. The volatilization, therefore, of the arsenic compound must be considered as incomplete.

To summarize, nitrates are entirely converted into fluorides by the vapors of hydrofluoric acid; with vanadates and arsenates the conversion is incomplete, while phosphates remain intact.

## 1. HYDROBROMIC ACID AND NITRATES.

Apparently no change occurs when these compounds are brought together in the cold. When gently heated aqueous vapor and bromine appear. In the course of half an hour the conversion into bromide is finished.

*Experiment.*—0.1887 gram of sodium nitrate gave 0.2286 gram of sodium bromide, instead of the theoretical 0.2273 gram.

## 2. HYDROBROMIC ACID AND PHOSPHATES.

Not even traces of phosphoric acid were expelled on heating sodium pyrophosphate in an atmosphere of hydrobromic acid.

## 3. HYDROBROMIC ACID AND VANADATES.

Sodium vanadate was acted upon in the cold. It became brown in color, and when the temperature was raised to almost 300° C., vapors escaped and condensed to an oily, reddish liquid beyond the heated portion of the tube. By the continued action of the acid this liquid acquired a green color, and small, green-colored crystals appeared. After the lapse of half an hour the liquid had completely solidified to a mass of radiating needles, having a beautiful green color. Several analyses of this compound showed the presence of 59.40 per cent. bromine and 14.65 per cent. vanadium, which would closely approximate the formula  $V_2O_5 \cdot Br_3 \cdot 3HBr \cdot 7H_2O$ , requiring 58.91 per cent. bromine and 15.02 per cent. vanadium. That such an oxybromide is not improbable may be inferred from the fact that Ditte (*Comptes rendus*, 102, 1310) prepared the compound  $V_2O_5 \cdot Br_2 \cdot 2HBr \cdot 7H_2O$ , by boiling vanadic oxide ( $V_2O_5$ ) with hydrobromic acid. It required 53.51 per cent. bromine and 17.06 per cent. vanadium. The conversion into bromide was not complete.

## 4. HYDROBROMIC ACID AND ARSENATES.

Quite a distinct reaction was evident with pure, dry, sodium pyroarsenate even in the cold. The salt assumed a dark-grey color. When a gentle heat was applied to it vapors were expelled; these condensed in the anterior portion of the tube to a pale-yellow, oily liquid, soluble in water. The temperature at which the reaction was carried out did not exceed 300° C. The boat contained pure sodium bromide.

*Experiment 1.*—0.5440 gram of pyroarsenate gave 0.6335 gram of sodium bromide, instead of 0.6331 gram, the theoretical quantity.

*Experiment 2.*—0.4277 gram of pyrophosphate gave 0.4984 gram of sodium bromide, while theory requires 0.4981 gram.

With this complete, quantitative expulsion of arsenic, and the non-volatilization of phosphoric acid before us, we next proceeded to the separation of the two acids, both being present as sodium pyro-salts.

*Experiment 3.*—0.1572 gram of sodium pyroarsenate and 0.1897 gram of sodium pyrophosphate were mixed and gently heated in hydrobromic acid gas. The phosphate remaining in the boat, when determined and calculated into pyro-salt, equaled 0.1903 gram. As it was free from arsenic, we did not estimate the arsenic contained in the receiver.

Through both hydrobromic acid and hydrochloric acid vapors, acting upon a mixture of arsenates and phosphates, a separation of the two acids may be effected.

The succeeding experiments relate to the conduct of nitrates, arsenates, and phosphates toward hydriodic acid gas. This was prepared by dropping water upon a mixture of amorphous phosphorus and iodine. It was carefully dried before it came in contact with the salts.

#### I. HYDRIODIC ACID AND NITRATES.

Sodium nitrate was changed by the gas into iodide. One approximate result may be given :

0.1039 gram of sodium nitrate gave 0.1886 gram of sodium iodide, instead of the theoretical 0.1833 gram.

Not one experiment could be completed, since explosions of considerable violence invariably occurred. A dark sublimate, apparently iodine, appeared in the tube, and after the lapse of a quarter of an hour a flash of fire ran through the tube, accompanied by a loud report. Not succeeding in finding a method to prevent this, further work was abandoned. These explosions



were doubtless due to the production of some unstable derivative of nitrogen and iodine.

Phosphates were not altered by contact with hydriodic acid gas.

## 2. HYDRIODIC ACID AND ARSENATES.

Sodium pyroarsenate was employed. In the cold the acid gas produced a change. Thus, 0.1592 gram of pyro-salt gave 0.2672 gram of sodium iodide, instead of 0.2689 gram. The arsenic volatilized, determined, and calculated into pyro-salt gave 0.1583 gram instead of 0.1592 gram. As explosions occurred in all the trials made we concluded to abandon the study.

It may not be uninteresting to present a scheme of the elements, composing Group V of the periodic system,

Nitrogen	Phosphorus	Arsenic	Antimony	———	Bismuth
14	31	75	120	164?	208
	Vanadium	Columbium	Didymium		Tantalum
	51	94	142		182,

and briefly review their deportment so far as known, when acted upon by the gaseous haloids. Nitrogen is fully expelled by all of them from nitrates. Phosphorus, existing as phosphates, apparently is absolutely uninfluenced and remains unaltered in the salts with which experiments were tried. Arsenic is only partially volatilized from arsenates by hydrofluoric acid gas, but is completely removed by any one of the remaining haloid acids. Antimony is fully expelled from antimonates by hydrochloric acid gas. No experiments have been tried with bismuth. Hydrofluoric and hydrobromic acid gas volatilize vanadium in part, while its removal from sodium vanadate by hydrochloric acid gas is complete. We have no knowledge of the action of hydriodic acid. Columbium yields volatile products with both hydrochloric and hydrobromic acid vapors. Didymium has never been subjected to this treatment. Tantalum is but slightly affected by the vapors of hydrochloric acid, although it has long been known that both the oxide of columbium and that of tantalum are volatilized to a marked degree when heated with aqueous hydrofluoric acid.

## SEPARATION OF SOLID AND LIQUID FATTY ACIDS.

BY L. DE KONINGH.

Received June 3, 1895.

THE April number of this Journal (289-295) contains a criticism, by Twitchell, of some processes for the separation of solid and liquid fatty acids. Being joint author with Muter of the process referred to on page 290, I wish to make a few observations.

The author states that he carefully carried out Muter's instructions in all important details. I beg to differ from him. We work directly on the fat and not on the fatty acids isolated therefrom. We do not *boil* with ether to dissolve the lead oleate, and after having taken the trouble to expel the ether by means of a current of carbonic acid we do not undo any good this may have done by passing a current of air, but add the Hübl solution directly, as we know the weight of the oleic acid by a previous titration. I feel sure, however, that there is a deal of exaggeration about all this danger of oxidation.

The lead oleate is precipitated as a bulky semi-fused mass which soon solidifies, and if ever so sensitive to oxygen can only be affected very superficially. When dissolving in ether the flask is nearly filled and the little air remaining is practically expelled by ether vapor, so that the few cc. of oxygen left certainly cannot cause a great oxidation. Even on filtering, the air is not likely to act much on a liquid which is always in an active state of evaporation and consequently repels the air. I feel sure that lead stearate and palmitate are insoluble in ether; then when carrying out the separation from the oleate, there soon comes a time when the filtrate no longer colors with ammonium sulphide. The author's suggestion, that it may be more soluble in ether containing lead oleate, is not supported by my own experience. Then Muter and I have stated in the *Analyst*, 15, 49, that the liquid acid from tallow gives practically the iodine figure of pure oleic acid. For lard acid we found, however, ninety-three to ninety-four per cent., and I am pleased to see Twitchell's confirmation of this figure.

As gold alloys containing too little silver cannot be parted by means of nitric acid, so the separation of lead oleate from lead stearate fails if too little of the former is present. I published, two years ago, a short article in the *Chem. News*, **66**, 259, dealing with this subject, and refer to the same.

### ACETIC ACID IN VINEGAR.

BY ALBERT R. LEEDS.

Received May 21., 1895.

RECENTLY, having occasion to determine the acetic acid in many samples of vinegar, I was surprised to find how vague and unsatisfactory are the directions relating to this simple matter in many text-books and manuals for public analysts.

One of the latter recommends that fifty cc. of vinegar should be used and the titration performed with soda, no particular strength or indicator being mentioned. Another, in general terms, calls attention to the fact that only approximate results can be obtained with soda, its acetate having a feeble alkaline reaction. The indicator, in the presence of which it so reacts, is not stated. Sutton's Volumetric Analysis calls attention to the necessity of substituting phenolphthalein for litmus, the acetates of the alkalies and alkaline earths having a perfectly neutral reaction to the former. He further adds that colored vinegars may be so titrated even when highly diluted.

Beginning with twenty-five cc., which I found at once to be much too large a quantity, and using seminormal acid soda as a convenient strength of alkali, I presently reduced the volume of vinegar to ten cc. and finally to five cc. When this was diluted with fifty cc. of water in a white porcelain dish, and phenolphthalein was used as indicator, the end reaction was satisfactory, except in the case of highly colored vinegars. In these it is not sharp. Nor can litmus paper or litmus solution be satisfactorily used with them. Litmus gives not only a lower reading, but lower by a very variable amount in different vinegars. Sixteen samples tested as above described gave percentages ranging from 2.63 per cent. to 5.65 per cent., with a mean of 4.49. A mixture made up of twenty-five cc. of each, gave 4.44 per cent. The color of these samples was white to dark brown.

According to Sutton, Pettenkoffer titrates vinegar with a known excess of baryta and estimates the excess with decinormal nitric or oxalic acid by the help of turmeric paper.

Thinking that baryta might give a sharper reaction, though not discerning any advantage in the use of decinormal oxalic or nitric acid, I used an approximately decinormal baryta solution with phenolphthalein and decinormal hydrochloric acid. The results agreed to 0.01 per cent. with those obtained with soda, and ordinarily the latter would be the more convenient and preferable reagent.

Sutton recommends as a process applicable in all cases and however dark the vinegar may be, the method of C. Mohr, which consists in adding to a known quantity of the vinegar a known excess of barium or calcium carbonate in fine powder. Pure calcium carbonate, he states, is preferable, as it dissolves more readily.

In his excellent manual on "Foods" page 518, Blyth adds: "If absolutely accurate determinations are required, it is best to add an excess of pure calcium carbonate to a known weight; the liquid is boiled, filtered, and the residual carbonate dissolved in slight excess of normal hydrochloric acid and titrated back with soda and cochineal. From the amount of carbonate thus found to have been unacted upon, the total acidity is calculated."

This process failed entirely in my hands; I took fifty cc. of the vinegar and added two and a half grams of pure precipitated calcium carbonate in fine powder. The flask was corked loosely and shaken many times each day during the course of six days, at the end of which time the contents were still acid. Also, the flask was gently heated at intervals some five to six hours in all. The acetic acid still remaining, after filtering off the calcium carbonate, amounted to nine-tenths per cent. The figure calculated from the residual carbonate corresponded to 3.64 per cent., or a total of 4.54 per cent. as against 4.44 per cent., found directly with soda.

Regarding the amount of vinegar as too large and the difficulty as probably due to the slowness with which a very dilute solution of acid decomposed the carbonate towards the end of the reaction, I then treated ten cc. with excess of carbonate for

two hours under a return-condenser. This was somewhat more successful, the liquid containing 0.72 per cent. and the figure calculated from the residual carbonate corresponded to 3.85 per cent.—a total of 4.57 per cent.

The true percentage being thus rendered very doubtful, I then had recourse to another recommended by Blyth. He states, page 517, that the strength may be accurately estimated by distilling 110 cc. until 100 cc. have been drawn over, *i. e.*, ten-elevenths." The 100 cc. will contain eighty per cent. of the entire acid present in the 110 cc., and may be titrated; or the specific gravity of the distillate may be taken and the strength found from the following table: "A trial by this method yielded a distillate with specific gravity of 1.055 at 15°, corresponding in the table given to 4.25 per cent.; in one trial, the distillate should by titration, 4.23 per cent., in another, 4.24. Assuming for reasons stated below, that the correct percentage was 4.43, these figures correspond to ninety-six per cent. of the acid instead of eighty.

The method of distillation was then varied in the following manner: Ten cc. were diluted with fifty cc. of water in a small retort the neck of which was inclined upward and then bent downward to join the condenser. The distillation was continued until about two cc. remained in the retort when another fifty cc. of water was added and the distillation repeated—in all four times. The distillates had a faint acetous, mingled with a pronounced hop-like odor, on adding silver nitrate they presently darkened and on standing threw down a black deposit. They contained:

1.	3.73	per cent. of acid, equivalent to 83.2 per cent. of total.
2.	0.54	" " " " " 12.1 " " "
3.	0.081	" " " " " 1.8 " " "
4.	0.041	" " " " " 0.9 " " "

During this long process I had obtained only 4.39 per cent. acid or ninety-nine per cent. of the total.

The distillation was repeated in the same manner, using ten cc. of vinegar and fifty cc. of water in three successive additions, but the vinegar had previously been strongly fortified with phosphoric acid. One trial gave 4.507 per cent. acid, another 4.514.

The distillates gave no reaction for chlorine, and possibly the high figure was due to the presence of a little acetate.

Finally, in order to get rid of the disturbing influence of the coloring matters the following method was adopted. Fifty cc. of vinegar with fifty cc., of water and a drop of phenolphthalein were titrated with decinormal baryta, the latter being added to three cc. in excess, and then followed by five cc. of decinormal sulphuric acid. Whether the precipitates were allowed to settle in the cold or with warming, appeared to make no difference in the results, the coloring-matters being carried down very nicely. In one trial the precipitate was filtered off and thoroughly washed before titrating back with acid: in another, the assay was made up to 100 cc. in a graduate and twenty-five cc. were pipetted off and titrated. The former corresponded to 4.48 per cent., the latter to 4.52 per cent. The bulk of the precipitate was approximately one cc., and making the requisite correction gives us 4.48 for the latter result also.

These figures being higher than those obtained directly, I then went back to the use of turmeric, so highly recommended by Pettenkofer, and obtained 4.43 per cent. With great care in the observation of the first brown ring which forms in the presence of the slightest excess of baryta, when a drop of the titrated solution is brought upon turmeric paper, the end reaction can be detected with certainty. The reading is lower than that with phenolphthalein and may be relied upon even with highly colored vinegars. For ordinary purposes, however, the latter indicator with decinormal soda is adequate.

---

### NEW BOOKS.

AN ELEMENTARY COURSE IN EXPERIMENTAL AND ANALYTICAL CHEMISTRY. BY JOHN H. LONG, M.S., Sc.D., PROFESSOR OF CHEMISTRY AND DIRECTOR OF THE CHEMICAL LABORATORIES OF THE SCHOOLS OF MEDICINE AND PHARMACY OF NORTHWESTERN UNIVERSITY. pp. 507. Chicago: E. H. Colegrove & Co.

This book considers three subjects. Part I, covering 275 pages, is devoted to experimental chemistry. The first chapter presents experiments in crystallization, in distillation, and those

that show the difference between physics and chemistry. In the second chapter, oxygen, hydrogen, and their compounds are considered. The halogens and their derivatives constitute the third chapter. At this point elements and compounds, as well as the use of symbols, are discussed. Nitrogen and the atmosphere are the subjects of experimentation in chapter four, while the fifth, sixth, and seventh chapters are occupied by the other frequently occurring non-metals and their derivatives. Seven chapters follow; in them facts relating to the more important metals are presented in simple experiments. Analytical tests follow each metal. Combining weights, the atomic hypothesis, and valency are considered immediately after the metal magnesium. It may be inferred from this that the author advocates first giving to the student an abundance of facts before deducing theories or entering upon a discussion of fundamental principles. This thought is constantly before the reader throughout the entire book. The explanations accompanying the numerous experiments in Part I are clear and to the point. It must be admitted that the author has presented his subject in such a manner that good will result. Part II (twelve chapters) is given to qualitative analysis. The subject-matter is not exhaustive, but here, as in Part I, types are presented to the student. These he works out in detail, being assisted in his efforts by valuable explanatory remarks on the part of the author. Part III considers the elements of volumetric analysis. The examples selected for work are typical and cover a wide field. Recent methods of value have not been overlooked. In this section, as in the two preceding sections, the author has presented all the subject-matter in a very clear style. In short, after careful inspection of the book one lays it down with the conviction that it possesses great merit; it is an excellent book and worthy of commendation.

EDGAR F. SMITH.

ELEMENTS OF MINERALOGY, CRYSTALLOGRAPHY AND BLOWPIPE ANALYSIS. BY ALFRED J. MOSES AND CHAS. L. PARSONS. pp. 342, with illustrations. New York: D. Van Nostrand Co., 1895.

This work, as indicated in its preface, is mainly intended for use as a text-book. It is divided into four parts: I. Crystallog-

raphy; II. Blowpipe Analysis; III. Descriptive Mineralogy; IV. Determinative Mineralogy.

The authors have given considerable space to crystallography, having devoted about one-fourth of the entire volume to the subject. The text is well written and fully illustrated.

In part II, after a chapter devoted to the apparatus, flame, etc., there is given a detailed description of the "Operations of Blowpipe Analysis," the reagents employed, and the results obtained in the various manipulations. This is followed by a series of "Useful Tests with the Blowpipe" on all of the principal elements. A valuable feature of this last chapter is a list of "Interfering Elements," which follows tests given for each element and in which directions are given for obtaining the proper reactions. The section is concluded by a chapter on "Schemes for Qualitative Blowpipe Analysis."

Part III, on Descriptive Mineralogy, occupies the major part of the book. The two first chapters treat of the physical characters and chemical composition of minerals. While the definitions of terms are clear and concise, they are in a few cases abridged to incompleteness and explanation of the optical and magnetic properties are omitted entirely.

The remaining chapters describe the various minerals under the heads of the elements forming their principal component parts. A distinguishing and most useful feature of this part of the work are the general remarks at the beginning of each chapter concerning the economic uses of most of the important minerals and ores.

The book would be more useful as one of reference, particularly to the analyst, if more attention had been given to the percentage composition. Many minerals have it in full, others only partially, while not a few have the formula only given.

Part IV consists of a number of tables of the usual tests for the rapid determination of minerals.

The arrangement of the book as a whole is excellent, and although the subject matter has been largely condensed, the elimination of less important details has made it much more practical than text books usually are, and it should be found useful to the professional mineralogist and chemist.

H. B. BALDWIN.



# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

---

### AMMONIUM PHOSPHOMOLYBDATE AND THE REDUCING ACTION OF ZINC IN THE REDUCTOR.

BY ANDREW A. BLAIR AND J. EDWARD WHITFIELD.

Received August 7, 1895.

**A**MONG the problems presented to the sub-committee on Methods of the International Steel Standards Committee, in the choice of a method for the determination of phosphorus in steel, none seemed more important than those involved in the composition of ammonium phosphomolybdate, and the reducing action of zinc on the molybdic acid of this salt under different conditions. The object of this investigation was to present data for the settlement of this question.

#### COMPOSITION OF AMMONIUM PHOSPHOMOLYBDATE.

In the preparation of ammonium phosphomolybdate the method usually followed was to precipitate the salt by adding a solution of microcosmic salt to a solution of ammonium molybdate in nitric acid; but Doolittle and Eavenson<sup>1</sup> showed that ammonium phosphomolybdate precipitated from a solution containing a large excess of ferric nitrate had essentially the same composition as that obtained by following the usual method of procedure.

In the investigation which we have made, we prepared a number of samples under different conditions and made careful analysis of each as a basis for our work.

<sup>1</sup> This Journal, 16, 234.

*Sample 1.*—Prepared by dissolving twenty grams of steel free from arsenic in nitric acid, adding twenty-five cc. of a saturated solution of microcosmic salt, evaporating to dryness, heating until the ferric nitrate was decomposed, dissolving in hydrochloric acid, diluting, filtering, evaporating to syrupy consistency, and then evaporating three times with excess of nitric acid to remove the hydrochloric acid. The solution was diluted to one liter, heated to about 60° C., and poured into one liter of molybdate solution. The precipitate was allowed to settle, the supernatant liquid was decanted, and the precipitate was washed by decantation with water containing one per cent. of nitric acid and finally filtered, washed, dried, removed from the filter, and heated to 150° C. for five hours.

*Sample 2.*—Prepared by partially neutralizing the first decantation from sample 1, adding twenty-five cc. more of the same microcosmic salt, washing, and drying the precipitate as above.

*Sample 3.*—Prepared by pouring a solution of microcosmic salt acidulated by nitric acid into molybdate solution, washing with water containing one per cent. of nitric acid, and filtering. A portion of this precipitate was dried at 150° C. for eight hours for sample 3.

*Sample 4.*—Prepared by taking a second portion of the precipitate above, washing with ice-water and drying over potassium hydroxide at the ordinary temperature for three months.

*Sample 5.*—Prepared by taking a third portion of the same precipitate, washing again with water containing one per cent. of nitric acid, and drying in the same manner as sample 4.

*Sample 6.*—The same as sample 5, but digested and washed before drying with water containing five per cent. of nitric acid.

*Sample 7.*—The same as sample 5, but digested and washed with water containing ten per cent. of nitric acid.

*Sample 8.*—Prepared by dissolving ferric oxide (obtained by igniting pure ferric oxalate) in hydrochloric acid, adding five per cent. of pure phosphoric anhydride, evaporating off the hydrochloric acid with nitric acid, heating to 80° C., adding an

excess of molybdate solution at 20° C., shaking in a large flask for three minutes and washing with water containing one per cent. of nitric acid. After thorough washing, the precipitate was digested with consecutive portions of water, containing varying amounts of nitric acid and with water containing nitric acid and ammonium nitrate. Then after standing two months with half a liter of water, containing five per cent. of nitric acid, it was filtered, washed with water containing five per cent. of nitric acid, and heated to 100° C. for five hours.

*Sample 9.*—Prepared from the same reagents, and in the same manner as sample 8. Washed by decantation with water containing five per cent. of nitric acid, dried at 100° C. for eight hours.

*Sample 10.*—Prepared and washed in the same manner as sample 9, but dried at 100° for twelve hours.

The methods employed in the analyses of these samples are the usual ones except that for the determination of water, and a general description will be sufficient.

As the salt is very hygroscopic the samples were in all cases placed in drying tubes with glass stoppers, heated to the temperature indicated, cooled over fused potassium hydroxide, and weighed out by difference.

#### DETERMINATION OF PHOSPHORIC AND MOLYBDIC ACIDS.

About two grams of the salt was weighed out by difference into a beaker, dissolved in twenty-five cc. of ammonia (0.96 sp. gr.) transferred to a carefully calibrated half liter flask and diluted to the mark with water. The solution was thoroughly mixed by pouring it into a dry beaker and back into the flask several times. By means of a pipette, which had been carefully tested against the flask, 100 cc. (containing about four-tenths gram of the salt) was measured into a beaker for the estimation of the molybdic acid, and 200 cc. (containing about eight-tenths gram of the salt) was measured into another beaker for the estimation of the phosphoric acid. To the latter was added, drop by drop, ten cc. of magnesia mixture with constant stir-

ring, then fifty cc. of ammonia and the precipitated ammonium magnesium phosphate was allowed to stand over night. The precipitate was filtered, washed with ammonia water, dissolved on the filter in dilute hydrochloric acid, made slightly alkaline with ammonia, ammonium sulphide added, the solution acidulated with hydrochloric acid and hydrogen sulphide passed through the hot solution for half an hour. The precipitated molybdenum sulphide was filtered off, the filtrate was boiled to expel hydrogen sulphide and the ammonium magnesium phosphate reprecipitated as before. This precipitate was filtered off, burned and weighed as magnesium pyrophosphate, and the phosphoric acid and phosphorus calculated in the usual way.

The solution for the determination of molybdic acid was diluted to about three-fourths of a liter with hot water, heated to boiling, slightly acidulated with acetic acid and a boiling solution of lead acetate (containing about three grams of the salt) was added. After boiling for about fifteen minutes the precipitate was allowed to settle, decanted through an asbestos filter on a Gooch crucible, washed thoroughly by decantation with hot water, transferred to the crucible, dried at  $120^{\circ}\text{C}.$ , and weighed as the mixed lead phosphate and molybdate.

The percentage of the mixed salts was calculated and from this amount was subtracted the percentage of lead phosphate found by multiplying the percentage of phosphorus previously found by 13.086. The difference (lead molybdate) multiplied by 0.39242 gave the percentage of molybdic acid.

#### DETERMINATION OF AMMONIA.

About one and a half to two grams of the salt was weighed out into a funnel inserted in the neck of a fractional distillation flask and washed down into the flask with water. The flask was fitted with a stopper carrying a bulb tube with a glass stop-cock. The side tube of the flask was fitted into a glass condenser to the lower end of which was attached one arm of a large bulb U tube containing ten cc. of hydrochloric acid and twenty cc. of water. The other arm of the U tube was fitted with a small calcium chloride tube, containing broken glass moistened with water. Fifty cc. of pure potassium hydroxide (1.27 sp.

gr.) was admitted to the distillation flask through the bulb tube, and the ammonia was distilled over. The contents of the U tube were transferred to a beaker, platinic chloride added, and the ammonia determined in the usual way.

#### DETERMINATION OF WATER.

The determination of water in ammonium phosphomolybdate offered unexpected difficulties. After repeated trials to get satisfactory results by heating the salt with sodium tungstate the following method was adopted :

At the middle point of a tube of hard glass 200 millimeters long, and nineteen millimeters in diameter was fused at right angles a tube thirty-seven millimeters long and nine millimeters in diameter. In the small tube a thermometer was fitted with sheet asbestos. The bulb of the thermometer extended a short distance into the large tube. The tube was placed in a horizontal position across the ring of an iron retort holder, the middle of it being protected by a piece of sheet copper three inches long bent around it, but separated from it by sheet asbestos. The ends of the tube were fitted with perforated corks, one carrying a small glass tube for the passage of dry air, and the other a U tube filled with calcium chloride. A porcelain boat sixty-two millimeters long and twelve millimeters wide was provided to hold the salt.

The stand holding the tube now closed with solid stoppers was placed near the balance case, about two grams of the salt was weighed out by difference into the boat which was immediately placed in the tube, and the latter closed by the corks. It was then placed in position, the perforated corks substituted for the others and a current of dry air passed through while the tube was heated by a Bunsen burner until the thermometer registered 250° C. The increase in weight of the calcium chloride tube gave the amount of water.

The only danger apprehended was that of decomposing the salt and liberating its ammonia, but careful experiments made by passing the air over the salt heated to 250° C. and into Nessler's solution showed that no trace of ammonia was given off.

The results of the analysis of the samples are as follows :

Sample.	Phosphoric acid. Per cent.	Molybdic acid. Per cent.	Ammonium oxide (NH <sub>4</sub> ) <sub>2</sub> O. Per cent.	Water. Per cent.	Ratio of Phos- phorus to 100 molybdic acid.
1	3.79	91.88	3.33	1.02	1.799
2	3.79	91.63	3.39	1.30	1.805
3	3.80	91.67	3.34	1.22	1.810
4	3.59	88.06	3.36	5.02	1.778
5	3.63	89.07	....	....	1.786
6	3.57	86.44	....	....	1.802
7	3.56	86.89	....	....	1.789
8	3.73	91.37	2.64	1.96	1.780
9	3.79	92.33	3.12	0.71	1.790
10	3.81	91.96	3.03	1.17	1.807
Average for the ten samples,					1.7946

These results are sufficient to show remarkable uniformity in the composition of ammonium phosphomolybdate precipitated under varying conditions and may be considered as practically answering the question as to the effect of the presence of ferric nitrate in the solution from which the precipitation is effected.

There are two points worthy of remark in these results. First, the variation in the amounts of water in the different samples, and second. the variation in the amounts of ammonia.

The explanation of the first point is found probably in the temperature of drying, that of the second in the washing of the precipitated salt. Sample 8, which was digested for a long time with dilute nitric acid, had lost most ammonia. This is borne out by the fact that the ammonia can all be destroyed by digestion with aqua regia and phosphomolybdic acid crystallized out from the solution. In this connection the following table of calculated composition compared with results obtained by analysis may be of interest :

## SAMPLE 10.

		Theory. Per cent.	Actual determination. Per cent.
24 MoO <sub>3</sub> .....	3456	91.19	91.96
P <sub>2</sub> O <sub>5</sub> .....	142	3.74	3.81
3 (NH <sub>4</sub> ) <sub>2</sub> O .....	156	4.12	3.03
2 H <sub>2</sub> O .....	36	0.95	1.17
	4790	100.00	99.97
Phosphorus ratio .....		1.794	1.807

## SAMPLE 4.

		Theory. Per cent.	Actual determination. Per cent.
24 MoO <sub>3</sub> .....	3456	87.45	88.06
P <sub>2</sub> O <sub>5</sub> .....	142	3.59	3.59
3 (NH <sub>4</sub> ) <sub>2</sub> O .....	156	3.95	3.36
22 H <sub>2</sub> O .....	198	5.01	5.02
	3952	100.00	100.03
Phosphorus ratio .....		1.794	1.778

The last trace of water seems to go off between 150° and 250° C., but the samples having been prepared and analyzed after drying at or below 150° C it was not deemed necessary to prepare the anhydrous salt especially as it is very hygroscopic. In view of the fact that the variation in the ratio of molybdic acid to phosphorus is so small (the average of the ten samples being 1.7946) we may without hesitation adopt the theoretical ratio of 1.794.

Samples 4, 5, 6, and 7 were prepared to test the accuracy of the statement made by Hundeshagen<sup>1</sup> that the precipitated ammonium phosphomolybdate washed with dilute acid and dried in a desiccator over calcium chloride and potassium hydroxide had the composition



Actual tests of these samples made by dissolving weighed amounts in a standard solution of potassium hydroxide and titrating back with standard nitric acid gave the following results:

	Standard alkali required to neutralize one gram of salt.
No. 3 .....	130.53
" 4 .....	119.14
" 5 .....	121.25
" 6 .....	123.59

Sample 7 was unfortunately used up in the preliminary analysis and none remained for this test, but as No. 3 was heated to 150° C., and the others were dried as described above, No. 4 having been washed with water, No. 5 with one per cent. nitric acid, and No. 6 with five per cent. nitric acid the results do not seem to bear out Hundeshagen's statement.

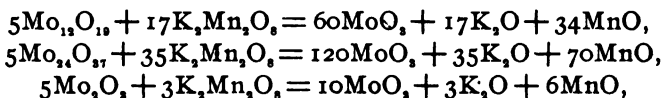
<sup>1</sup> *Chem. News*, 60, 168.

It was hoped also, that the neutralization (Handy's) method might offer some advantages over the reduction method for the determination of phosphorus in steel, but the hygroscopic character of the ammonium phosphomolybdate and the lack of agreement in the results obtained caused us to abandon this part of the investigation.

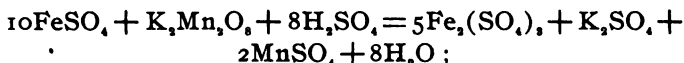
#### THE REDUCTION OF MOLYBDIC ACID BY ZINC.

When a solution of ammonium phosphomolybdate in ammonia is acidulated with sulphuric acid and the molybdic acid is reduced by metallic zinc it was claimed by Werncke that the reduction was not to the form  $\text{Mo}_2\text{O}_3$ , but to  $\text{Mo}_{11}\text{O}_{11}$ . This theory was adopted by Emmerton and has been generally accepted by chemists as the formula to be used in the determination of phosphorus by the reduction method. When Jones' reductor came into general use it was noticed that the green color of the reduced solution was more permanent and the oxidation with potassium permanganate was from this color and not from the port-wine color referred to by Emmerton. Babbitt<sup>1</sup> claimed that the reduction was to a point between  $\text{Mo}_2\text{O}_3$  and  $\text{Mo}_{11}\text{O}_{11}$ , but Noyes<sup>2</sup> claimed that the reduction was to  $\text{Mo}_2\text{O}_3$ .

The reactions may be indicated as follows for the subsequent oxidation by potassium permanganate :



then as



or one molecule  $\text{K}_2\text{Mn}_2\text{O}_8$  oxidizes ten molecules of iron to the ferric condition, and we have for the ratio of iron to molybdic acid 100 to 90.756 in the first case, to 88.163 in the second, and to 85.714 in the third.

In other words, we must multiply the value of the permanganate solution in iron by 0.90756, by 0.88163, or by 0.85714 according to the theory we adopt for the reducing action of zinc on the solution of ammonium phosphomolybdate.

<sup>1</sup> *J. Anal. Appl. Chem.* 7, 165.

<sup>2</sup> This Journal, 16, 553.



The differences are certainly too great to be disregarded, and it becomes necessary to decide which theory we must adopt.

We have, therefore, sought to discover in the following experiments, first, what conditions affect the reduction, and secondly, whether the methods in ordinary use are capable of giving uniform results.

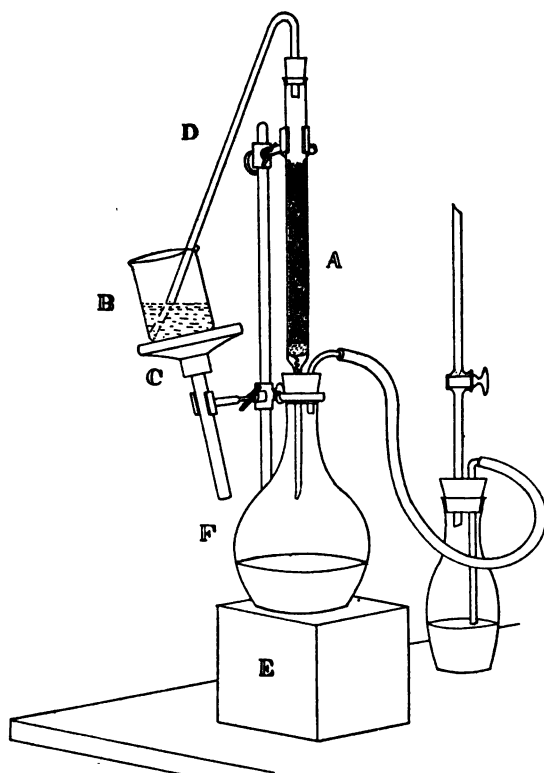
First, sample 10, containing 91.96 per cent. molybdic acid was selected for these experiments and a number of glass stoppered weighing tubes were filled with the carefully ground and dried salt. About two grams of the salt was weighed by difference into a beaker, dissolved in five cc. ammonia (0.96 sp. gr.) washed out into a half liter flask, diluted to the mark with distilled water, mixed by pouring back and forth into a dry beaker, and measured out by means of a twenty-five cc. pipette, carefully tested with the flask into beakers. Twenty cc. ammonia (0.96 sp. gr.) were added, the solution was acidulated with twenty-five cc. sulphuric acid (1-4) and passed through the reductor. The reduced solution was titrated with standard permanganate and the molybdic acid calculated by the proper formula.

The reductor shown in the accompanying sketch was used. This form of reductor was suggested by Mr. W. P. Barba of the Midvale Steel Co., a member of the sub-committee on Methods of the International Steel Standard Committee, and has been found most convenient.

In the bottom of the reductor tube A was placed a spiral of platinum wire, on top of this a piece of platinum gauze, a wad of glass wool six millimeters thick, and then a thin film of asbestos. The tube was filled with granulated zinc to within thirty-seven mm. of the top and a wad of glass wool twelve millimeters thick filling the diameter of the tube placed on top. This served to distribute the acid and to prevent the liberated hydrogen from spattering the solution on the upper part of the tube. The solution having been placed in the beaker B, the latter was placed on the stand C, and the tube D placed in position. The flask F having been attached, the block E was placed under it, and the pump having been connected the liquid was drawn over from B.<sup>1</sup> When the liquid in B was almost all

<sup>1</sup> See seq. for use of dilute sulphuric acid for washing.

drawn over, the sides of the beaker were washed down and then the beaker was filled with water, and when this was all drawn over, the stopper carrying the tube D was removed and the re-



ductor tube was filled with water to thoroughly wash out the top of the tube. The flask was removed, the end of the reductor tube washed into it, the sides of the neck of the flask washed down with water, and the reduced liquid was titrated in the flask.

In making a blank determination, the solution was made up as nearly as possible to the composition of the solution of the salt; *viz.*, twenty cc. ammonia, twenty-five cc. sulphuric acid (1-4) and water to the same volume.

In giving the results of our experiments, it seems unnecessary

to give all the figures as they comprise several hundred in number, extending over a period of six months. Only those illustrating the facts of interest are therefore annexed.

The most curious result obtained was in an effort to get the greatest possible reduction of the solution by repassing it through the reductor, heating it nearly to boiling after each passage. In the third passage, the solution instead of coming through green in color, was almost colorless and the green oxide of molybdenum was found deposited on the zinc in the reductor. In another attempt to reduce the molybdic acid by treating the solution in a flask with zinc in a current of hydrogen at a boiling temperature, redissolving the excess of zinc by sulphuric acid admitted through a funnel tube, allowing the solution to cool in the current of hydrogen after diluting by means of the funnel tube with boiled distilled water and titrating in the flask, the following results were obtained:

Weight of phosphomolybdate .....	0.08784 grams.
Volume of permanganate required .....	24.9 cc.-24.9 cc.
Molybdic acid on $\text{Mo}_2\text{O}_3$ theory.....	84.86 per cent.
“ “ “ $\text{Mo}_{24}\text{O}_{37}$ “ .....	87.28 “
“ “ “ $\text{Mo}_{12}\text{O}_{19}$ “ .....	89.85 “
“ “ “ Mo by grav. det .....	91.96 “

showing that the reduction was not even to  $\text{Mo}_{12}\text{O}_{19}$ .

A series of determinations was made to test the best rate of speed for passing the solution through the reductor, and for a column of zinc from two hundred to two hundred and fifty mm. no appreciable difference was noticed between a speed of two minutes and one of ten minutes for the passage of a solution made up in the usual way, except that it was necessary to follow the solution of phosphomolybdate by dilute sulphuric acid when the rate of speed was very slow to avoid leaving some molybdenum trioxide in the zinc. This precaution was finally made a part of every determination and the beaker which contained the solution to be reduced, was washed down with a hot solution of sulphuric acid (ten cc. of sulphuric acid (1-4) diluted to 100 cc.) and the operation was completed by washing with water. A speed of about two minutes was finally adopted with a hot solution. It was also found advisable to pour fifteen cc.

of sulphuric acid (1-4) into the titrating flask, before attaching it to the reductor.

The following results will illustrate the effect of dilution :

Weight of phosphomolybdate.	Volume of solutions in cc.	Permanganate required in cc.	MoO <sub>3</sub> by Mo <sub>24</sub> O <sub>37</sub> theory. Per cent.
0.03095	175	9.0	88.83
0.03095	175	0.2	90.80
0.06190	175	18.35	90.55
0.06190	175	18.40	90.80
0.15475	175	46.40	91.59
0.15475	175	46.35	91.49
0.03589	500	10.1	85.76
0.14356	500	42.6	90.64
0.07178	500	20.9	88.94
0.14356	250	43.1	91.71
0.07178	250	21.0	89.36
0.14356	125	43.05	91.60
0.07178	125	21.5	91.49
0.09720	50	29.1	91.45
0.09720	50	29.05	91.29
0.09720	75	29.2	91.77
0.09720	75	29.1	91.45

These results all point to the fact that it is desirable to have the solution sufficiently concentrated, and a volume of 100 cc. was finally adopted as being most satisfactory for general use and for weights of phosphomolybdate up to two-tenths gram. With greater amounts of phosphomolybdate it is necessary to increase not only the volume of the solution but also the amount of sulphuric acid in order to prevent the reprecipitation of the ammonium phosphomolybdate in the acid solution.

Many variations in the manipulation were tried, such as passing a small volume of dilute sulphuric acid through the reductor, following this with the solution of phosphomolybdate without allowing any air to pass in and completing the operation by washing with dilute sulphuric acid and water which had been boiled to expel the air, but no higher results were obtained, and we concluded that the reduction was practically to Mo<sub>2</sub>O<sub>3</sub>, and not to Mo<sub>2</sub>O<sub>5</sub>.

Secondly, to determine whether the methods in ordinary use would give results agreeing with these, it was determined to

send portions of this sample to the members of the sub-committee and also to Prof. Noyes and Mr. Doolittle. These samples were sent in the weighing tubes with the request that the tube be dried at  $100^{\circ}$  C. for about an hour and cooled in a desiccator. Then that about one gram be weighed out by difference, dissolved in ammonia, diluted to 250 cc. and portions of twenty-five cc. each measured off, acidulated and titrated in the usual manner; then that the results be returned in the following way; weight of phosphomolybdate used for the reduction, corrected volume of permanganate required for the oxidation, value of permanganate in iron. These returns were then calculated, giving the following interesting results.

MOO<sub>3</sub> IN SAMPLE 10 PHOSPHOMOLYBDATE.

	Mo <sub>2</sub> O <sub>3</sub> theory. Per cent.	Mo <sub>2</sub> O <sub>3</sub> , theory. Per cent.	Mo <sub>12</sub> O <sub>19</sub> theory. Per cent.	Gravimetric. Per cent.
Blair.....	88.91	91.45	94.14	91.96
Dudley .....	88.61	91.11	93.83	
Drown .....	88.68	91.21	93.90	
Shimer.....	88.22	90.74	93.41	
Doolittle (Job).....	90.47	93.05	95.80	
Noyes.....	89.95	92.52	95.25	
Average .....		91.68		91.96

May we not conclude from these results—

First, that the ratio of phosphorus to molybdic acid is 1.794?

Second, that the value of molybdic acid as compared with iron is 0.88163 according to the theory of reduction of the molybdic acid to Mo<sub>3</sub>O<sub>7</sub>?

## MOLYBDATE SOLUTION.

In the course of this investigation, our attention was naturally called to the stability of molybdate solutions and the composition of the yellow precipitate which forms sooner or later in nearly all these solutions.

This precipitate carefully collected, washed with dilute nitric acid and then with cold water and dried over sulphuric acid was bright orange colored and contained by analysis,

Molybdic acid.....	90.43
Water at $250^{\circ}$ C.....	9.61
Phosphoric acid .....	None
Ammonia .....	Traces

When heated the precipitate became white and was in fact molybdic anhydride. As ammonium phosphomolybdate is much less soluble in dilute nitric acid containing ammonium nitrate than in dilute nitric acid alone, we considered it possible that the excess of ammonium nitrate might be the cause of the instability of these solutions and an experiment showed this to be the case. We found that the solution prepared according to the following formula remained practically unaltered for several months and gave exactly the same results as a fresh solution when used for the determination of phosphorus in steel. The following is the formula and method of preparation:

One hundred grams of molybdic anhydride was thoroughly mixed with 400 cc. of cold distilled water and eighty cc. of ammonia (0.91 sp. gr.) was added. This completely dissolved the molybdic acid. The solution, after filtering to remove any silica or dirt, was poured into a mixture of 300 cc. nitric acid (1.42 sp. gr.) and 700 cc. water. The solution did not become very warm and there was very little tendency on the part of the molybdic acid to separate out during the mixing.

LABORATORY OF BOOTH, GARRETT & BLAIR,  
PHILADELPHIA.

## THE FERRATES.<sup>1</sup>

BY CLAUDE A. O. ROSELL.

Received August 2, 1895.

“ ‘WHO has first seen ferric acid?’ ” This question forms the pertinent title of a controversial article in the *J. Prakt. Chem.*, **32**, 448, and it is there stated that G. E. Stahl discovered that when saltpeter is ignited with iron and the mass is added to water, the caustic alkali resulting from the decomposition of the saltpeter holds a part of the iron in solution and produces an amethyst or purple color. He also stated that if dilute solutions of iron in nitric acid are poured in successive small portions into a strong solution of caustic potash the iron is dissolved on shaking, with a blood-red color.

While verifying the accuracy of the former I have not been able to reproduce the latter of these reactions. On its face it

<sup>1</sup> Read at the Brooklyn meeting.

looks so improbable that it must be believed that the statement is erroneous. Probably the nitric acid that Stahl used contained sufficient hydrochloric acid to make the reaction possible. Be this as it may, certain it is that the direction given by Stahl for making potassium ferrate in the dry way, through the ignition of saltpeter with iron, is sufficiently clear to be successfully followed, so that he is undoubtedly entitled to the credit of being the discoverer of ferric acid.

As recently as in Muir & Morley's edition of Watt's Dictionary of Chemistry, London, 1889, page 547, it is stated that "Stahl noticed in 1702 that a violet solution is obtained by fusing iron with saltpeter and washing with water or by adding a solution of iron in  $\text{HNO}_3$  to conc.  $\text{KOH}$  aq.," which shows that these two editors had nowhere found a correction of the erroneous statement of Stahl, nor has a correction been published by any one until now.

In 1802 potassium ferrate was rediscovered by Ekeberg, while fusing gadolinite, which is a silicate of yttrium, beryllium, and iron, with caustic potash. In this experiment the ferric oxide, of which the gadolinite contains sixteen per cent., was oxidized in the presence of caustic potash so as to form potassium ferrate. However, neither Stahl nor Ekeberg examined the character of the iron compound which resulted from the reaction with the caustic potash, either added or produced in the process, and which gave rise to the claret color observed.

When Fremy undertook an investigation of those compounds of the metallic oxides, in which the latter play the part of acid metallic anhydrides, he very soon rediscovered the solution of ferric oxide in caustic potash. In this solution he found that the oxide did not exist as ordinary ferric oxide,  $\text{Fe}_2\text{O}_3$ , but that it contained more oxygen than the latter, the quantity of oxygen contained corresponding roughly, or as closely as it was possible to analytically determine the constitution of an impure and somewhat variable body, such as barium ferrate, to the formula  $\text{FeO}_4$ , a result which has since been confirmed by J. Denham Smith and H. Rose.

The accounts of Fremy's work were published from time to time in a number of scientific periodicals, commencing with

January, 1841, when he states that the compound of oxide of iron and potash which is soluble in water corresponds in composition to the manganates, and in 1842 the new compound was called by him ferric acid, though the name had already been suggested by J. Denham Smith in *Phil. Mag. Ser. [3]*, **19**, 302.

Besides producing potassium ferrate by the methods of Stahl and Ekeberg, which were unknown to him, Fremy also obtained it by electrolyzing caustic potash with an anode of cast iron and also by introducing chlorine into a solution of caustic potash containing ferric hydroxide in suspension. In addition he produced this salt by heating iron with potassium dioxide.

In attempting to produce sodium ferrate by such processes as Stahl and Ekeberg had used to produce potassium ferrate he failed. Not only did Fremy fail in his attempts to produce sodium ferrate in the dry way, but there is not to be found in the literature of the subject any account of anybody else who has succeeded in doing so or who has ever suggested the possibility of its being accomplished. In fact the statement occurs in chemical literature that sodium ferrate cannot be made except in the wet way. Thus in Wurtz' *Dictionnaire de Chimie*, Volume I, Part 2, page 1413, the following is found: "Sodium ferrate is soluble in water and cannot be prepared except in the wet way."

Bloxam prepared a solution of sodium ferrate by adding bromine to a strong solution of caustic soda containing ferric hydroxide in suspension. This I have found a very quick and convenient method of producing a small quantity of a solution of sodium ferrate. I have also several times made the attempt to produce sodium ferrate by the addition of iodine to a solution of caustic soda holding ferric hydroxide in suspension, but no sodium ferrate was formed.

Bloxam also found that a solution of calcium ferrate may be produced by gently heating a solution of bleaching powder with a small portion of ferric chloride. On repeating this experiment I have found the process to be a very delicate one and that it often fails, although, if very carefully conducted a rose-red solution of calcium ferrate is formed. I thought that perhaps by the addition of lime to the bleaching powder solution the reac-



tion might take place more expeditiously. Such, however, was not the case, as a solution of calcium ferrate could never be produced when lime was first added to the bleaching-powder solution containing a small portion of ferric hydroxide in suspension.

It was first stated by Fremy and it has subsequently been repeated in the text-books that calcium ferrate, like barium ferrate, is insoluble in water. The experiment of Bloxam above referred to shows that this statement is not correct.

On preparing a solution of sodium or potassium ferrate allowing it to stand, it sometimes changes color from red to green. J. Denham Smith believed this green solution to be caused by some new iron compound, but Heinrich Rose showed that it was derived from manganese. The ferrate solution prepared contained a manganate. On standing, the ferrate decomposed while the manganate remained unchanged until at last only manganate remained, when the solution turned green. I have repeatedly verified the correctness of Rose's explanation.

In undertaking a course of investigation of the properties of ferric acid the following interesting problems presented themselves :

1. Production of sodium ferrate in the dry way.
2. Production of iron dioxide.
3. Decomposition of barium ferrate by metathesis so as to obtain in this way a normal ferrate containing no free alkaline hydroxide.
4. Determination of the constitution of the thioferrates.

#### I. PRODUCTION OF SODIUM FERRATE IN THE DRY WAY.

In the attempts to produce sodium ferrate in the dry way, ferric oxide, both dry and hydrated, was calcined with caustic soda, sodium carbonate, sodium nitrate, and with mixtures of sodium hydroxide and nitrate, and also with sodium nitrate and carbonate, but all in vain. The substitution of sodium chlorate for a part or all of the sodium nitrate was also tried but with no change in the result. Sodium dioxide was then tried, but at first without success. It was however observed that when the fused mass from this last experiment had been allowed to cool, on subsequent addition of water it became highly heated, and

it was suspected that while sodium ferrate had been produced by the reaction, that it was at the same time decomposed by the heat, resulting from the addition of the water, and it was believed that if this rise in temperature could be obviated the decomposition of the ferrate might be prevented. This theory was acted on and the mass resulting from the fusion of the ferric oxide and the sodium dioxide was treated with ice, and though some rise in temperature still followed it was much less than before, and sodium ferrate was obtained in solution. Thus the first problem had been successfully solved and sodium ferrate was for the first time produced in the dry way. There are two probable reasons why Fremy failed. In the first place, when using sodium nitrate this was to a great extent decomposed by the heat leaving behind sodium nitrite which is stable at high temperatures, and which, when the mass was dissolved in water served as a reducing agent, reducing the iron trioxide to the ordinary ferric oxide, while the nitrite itself, by oxidation, became converted into nitrate. When using caustic soda the cause of the failure was probably the heating of the mass on the addition of water, which heating has already been referred to.

## II. ATTEMPTED PRODUCTION OF IRON DIOXIDE.

The production of iron dioxide was of course the most important of the problems. The hope of accomplishing this result was the inciting cause of the investigation and a great number of experiments were conducted with this end in view.

As it is well known that chromium dioxide can be readily obtained by adding a solution of a chromic or chromous salt to a chromate it would seem at first sight that, having the iron monoxide and the trioxide, the iron dioxide might be easily prepared by an analogous reaction to the one above mentioned.

To produce a precipitate of iron dioxide from a solution of sodium ferrate, which is highly alkaline, the solution of the iron salt added would have to be alkaline. Such a solution may be made in many ways, such as by the addition of tartaric acid, citric acid, or glycerol, to a solution of a ferric salt and then adding a caustic alkali in excess, but in each case the organic solvent was oxidized before any precipitate was formed and so this method had to be abandoned.

The addition of barium ferrate to solutions of ferric chloride, both normal and basic, was tried with apparently good prospects of success as the barium went into solution as chloride, but at the same time oxygen and also chlorine were given off, so that the precipitate ultimately obtained consisted merely of ordinary ferric hydroxide. For the purpose of this experiment, the barium ferrate was just as good as normal sodium ferrate could this latter be produced; the barium ferrate decomposed the ferric chloride perfectly, so that if iron dioxide is capable of production, here the conditions of success seemed to be the best and yet the result of the reaction was only ordinary ferric oxide. Hence, it is quite certain that if iron dioxide can be made at all, it is a compound of such exceeding instability as to have decomposed as fast as formed.

### III. THE REACTIONS OF BARIUM FERRATE.

Of the ferrates the most stable, the one that can be prepared in the purest state and the most definite in composition is barium ferrate,  $\text{BaFeO}_4 \cdot \text{H}_2\text{O}$ , this formula having been determined by Fremy and H. Rose. Before barium ferrate has been allowed to dry it is decomposed by all the soluble acids, including carbonic acid. After it has once been allowed to dry in a desiccator it is not so easily decomposed, at least completely. If barium ferrate, which has not been allowed to dry, be suspended in water through which carbon dioxide is passed, it will be completely decomposed with the formation of barium carbonate and ferric hydroxide, oxygen being set free. From this decomposition it might reasonably be expected that iron dioxide would be formed just as manganese dioxide is formed on passing carbon dioxide through water containing barium manganate in suspension, but such is not the case. This experiment would also seem to indicate that neither a compound of iron, corresponding to a permanganate nor a compound corresponding to a bichromate exists. The result of passing carbon dioxide through water containing barium ferrate in suspension, with the object of obtaining new iron salts therefore carries with it two disappointments.

When barium ferrate has been thoroughly dried in a desicca-

tor it is readily attacked by acids, but complete decomposition is not readily effected in the cold even with dilute sulphuric acid, oxalic acid, formic or acetic acids. Hydrochloric acid decomposes it completely with the greatest readiness, chlorine being always set free. If barium chromate be digested with a solution of sodium ferrate, barium ferrate is formed and the solution changes color from red to yellow, due to the sodium chromate which has been formed. The reverse reaction never takes place. Thus, if barium ferrate is digested with a cold solution of an alkaline carbonate, sulphate or triphosphate, an alkaline ferrate is never formed, the solution remaining colorless. An alkaline sulphate will decompose barium ferrate that has not been dried with the formation of barium sulphate and ferric hydroxide, oxygen being set free. It thus appears that barium ferrate is one of the most insoluble salts known. It is strange that in none of the publications up to this time has the behavior of barium ferrate to neutral salts been referred to.

#### IV. THIOFERRATES.

Freymy states that on passing hydrogen sulphide through a solution of sodium ferrate a solution is obtained of a beautiful emerald color. He supposed that the sodium ferrate was converted into sodium thioferrate. On passing hydrogen sulphide through a solution of sodium ferrate I sometimes obtained the green solution described by Freymy and at other times not. Investigating the matter, I found that the green solution was obtained only when the original solution contained manganese. It appears then that on passing hydrogen sulphide through a ferrate solution containing a manganate the ferrate is reduced by the hydrogen sulphide, leaving the green manganate solution behind. If, on the other hand, the ferrate solution contains no manganese, on passing hydrogen sulphide through it, the red color disappears and a solution is obtained having a greenish yellow tinge, such as is obtained by digesting precipitated iron sulphide in a solution of an alkaline polysulphide, the greater part of the iron being precipitated as black sulphide. The supposed thioferrates must therefore be considered as mythical.

The only use so far suggested for the ferrates, is the produc-

tion of oxygen described in British Patent, No. 85, Jan. 10, 1886, to Brooman, a communication by Maréchal and Tessie du Motay, in which it is stated that potassium, sodium, and barium ferrate may be decomposed by a current of steam and subsequently reformed by the action of a current of air at high temperature.

Whether the ferrates resemble the chromates or manganates more is difficult to say. If a salt could be produced corresponding, either to the bichromates or the permanganates the question would of course be immediately decided. The extreme insolubility of barium ferrate, together with the solubility of calcium ferrate, as well as the instability of the dioxide, if it does exist, brings the ferrates closer to the chromates than the manganates. On the other hand the soluble ferrates can only exist in alkaline solutions, and in this respect they resemble the manganates. In their oxidizing power the ferrates still more closely resemble the manganates. It has already been stated that a ferrate will oxidize nitrites, tartrates and glycerol. The soluble ferrates are also decolorized or reduced by oxalates, alcohol, ether, ammonia, urea, and other soluble organic bodies with very few exceptions, such as, and notably, the acetates. They are decomposed also by some insoluble organic bodies, such as paper and insoluble carbohydrates, but most insoluble organic bodies, such as the paraffines and benzene, decompose them but very slowly.

To perform all the experiments on ferrates above referred to, sodium and potassium ferrate had often to be prepared. Of all the methods of making these salts the easiest is to pass chlorine through a strong solution of sodium hydroxide, containing ferric hydroxide in suspension. At one time I produced sodium ferrate on a scale never before attempted. Three kilos of sodium hydrate were dissolved in enough water to form ten liters of solution. To the solution were added 150 grams of ferric chloride, and the mixture stirred for a long time until the ferric hydroxide formed was all finely divided and evenly distributed throughout the solution. Through the mixture chlorine gas was then passed from a cylinder of liquid chlorine which had kindly been presented by my friend Dr. Rudolph Knietsch, one of the leading chemists of the Badische Anilin und Soda Fabrik of Ludwigs-

hafen, Germany. The operation was carried on very successfully, the chlorine gas passing through with great regularity, and in this manner a quantity of stock solution was prepared sufficient for all subsequent experiments.

It may here be stated that whenever an experiment is described above it has been actually tried for the purpose of making sure that the reaction indicated actually takes place.

The following is a summary of the errors which occur in the literature of ferric acid :

1. The direction for making potassium ferrate by adding iron nitrates to caustic potash, by Stahl.
2. The statement that on standing a solution of potassium ferrate changes color and turns green, made by J. Denham Smith.
3. The statement that calcium ferrate is insoluble in water, made by Fremy.
4. The direction for making thioferrates by passing hydrogen sulphide through a solution of a ferrate, by Fremy.
5. The allegation that sodium ferrate cannot be made except in the wet way, made by Wurtz.

Of these, the second error was corrected by H. Rose and the third by Bloxam, the other three having now for the first time been brought to light.

In the annexed bibliography are included only original articles, and when articles have been reprinted in different periodicals, only the first has been given. The full titles of the articles referred to have been perused, so that it is certain that they exist and relate to the subject-matter indicated.

#### BIBLIOGRAPHY.

1844. G. E. Stahl, 1702, referred to in *Journal für Praktische Chemie*, 32, 448, but a copy of Stahl's writings has not been attainable.

1802. Ekeberg, *Kongliga Vetenskapsakademiens Handlingar*, p. 68. *Uppllysning om Ytterjordens egenskaper i synnerhet i jemförelse med Berylljorden; om de Fossilier, hvori förstnämnde jord innehalles, samt om en ny upptäckt kropp af metallisk natur af A. G. Ekeberg.* (Description of the properties of yttrium oxide, especially in comparison with beryllium oxide, of the fossils, in which the former oxide is contained and of a newly discovered body of metallic nature by A. G. Ekeberg.)

1832. Bequerel, *Ann. Chim. Phys.*, [2] 51, 105: *De la cristallisation de quelques oxides métalliques.*

1841. Fremy, *Compt. Rend.*, 12, 23: Recherches sur l'action des peroxides alcalins sur les oxides métalliques.

1841. Poggendorff, *Ann. der Phys. Pogg.* 54, 371: Bildung der Eisensäure auf galvanischen Wege.

1841. J. Denham Smith, *Phil. Mag.*, [3] 19, 302: Experiments on the alleged conversion of carbon into silicon.

1842. Fremy, *Comp. Rend.*, 14, 442: Recherches sur les acides métalliques.

1843. H. Rose, *Ann. der Phys. Pogg.*, 59, 315: Über die Zusammensetzung der Eisensäure.

1843. J. Denham Smith, *Phil. Mag.* [3] 23, 217: On the Composition of an Acid Oxide of Iron (ferric acid).

1844. Fremy, *Ann. de Chemie*, [2] 12, 365: Recherches sur les acides métalliques.

1844. *Ann. der Phys. Pogg.* 52, 288: Wer hat die Eisensäure zuerst gesehen?

1844. *Prakt. Chem.*, 32, 448: Wer hat die Eisensäure zuerst gesehen?

1879. W. Foster, *Ber. d. chem. Ges.* 12, 846: Notiz über die höhern Oxyde von Eisen, Chrom, Mangan, und Wismuth.

1886. Bloxam, *Chem. News*, 54, 43: Lecture Experiment. The Ferates.

THE COLUMBIAN UNIVERSITY,  
WASHINGTON, D. C.

---

[CONTRIBUTION FROM THE LABORATORY OF THE LOUISIANA SUGAR  
EXPERIMENT STATION AND SUGAR SCHOOL.]

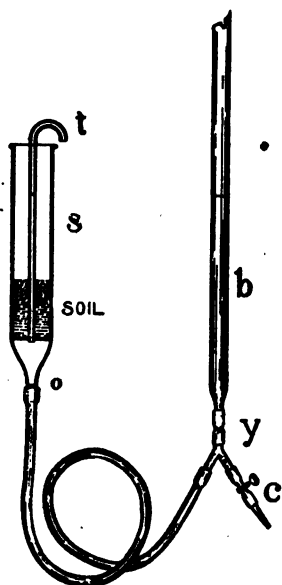
## A SIMPLE AND CONVENIENT APPARATUS FOR ESTIMATING THE WATER-HOLDING POWER OF SOILS.

BY J. L. BEESON.

Received June 3, 1895.

TO a fifty or 100 cc. plain burette is connected a glass Y tube by means of a piece of rubber tubing. To one of the forks is attached a bit of rubber tubing carrying a pinch-cock, and the other fork is connected with a small Stutzer extraction tube, having a zero mark scratched on its neck, by means of a stout piece of rubber tubing about two and one-half feet long. The apparatus is fastened in the clamp of an ordinary clamp-stand. A metallic disk, which will about fit the larger tube, is perforated with many small holes, the center with a larger hole that will admit the end of a piece of glass tubing, which is made firm by

fusing into the glass by means of a burner or blast lamp. The upper end of the tube, d t, is bent over so that the soil will not fall into it while filling the larger tube. Disks of filter-paper, of convenient size, are perforated with a cork borer, and one of



these is slipped over the glass tube down against the perforated disk, and held down by means of a rubber washer cut from a piece of small rubber tubing. The edges of the paper are folded under the disk so as to make it fit the tube well, and the whole slipped down to the bottom of the large tube. The apparatus, which is now ready for use, is very simple, and much more rapid and convenient, it is believed, than the one devised by Mr. Feulling as described in Dr. Wiley's book on soil analysis. The apparatus is filled with water, the

burette raised so as to cover the disk and filter-paper and then lowered. The excess of water will now run out of the filter-paper so that the reading will become constant within five minutes. Then by means of the pinch-cock c water is slowly drawn off until it stands at the zero mark on the neck of the tube o, and at zero on the burette. From twenty-five to fifty grams of soil, according to the water-holding power of the sample, is added to the large tube S, which is gently tapped until the soil is level. The burette is raised and the water gently forced into the soil from below until it forms a level above the soil. From the height of the column of water in the air-tube t the amount of pressure may be seen. The burette is then lowered and the water runs out of the soil by gravity alone, since the space below the disk is supplied with air through the tube t. When there is no more rise of water in the tube, which requires about fifteen to



twenty minutes, the burette is raised until the water stands at the zero mark 0 in the tube, when the number of cc. of water absorbed by the soil is read on the burette. The whole time for an analysis need not exceed thirty or forty minutes. The pinch-cock on the Y tube is most convenient in bringing the water to the zero marks on the tube and burette before adding the soil. The apparatus may be obtained of Kæhler and Martini, Berlin.

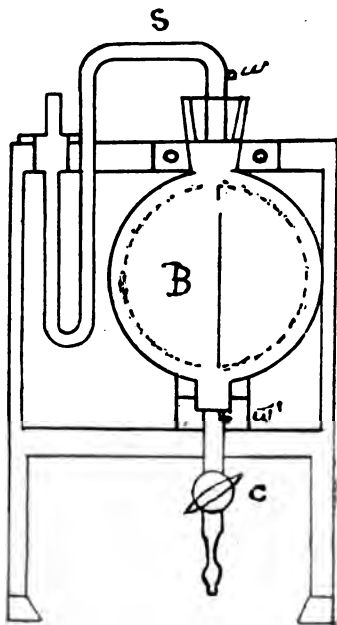
### A MODIFICATION OF HINMAN'S EXPLOSION PIPETTE.

By AUGUSTUS H. GILL.

Received August 7, 1895.

THIS pipette was devised to permit the use of all the residue, sixty cc., remaining after an illuminating gas had been analyzed by the Hempel apparatus, in mixing with oxygen for explosion.

It consists of a bulb, B, eleven to twelve cm. in diameter, of about 250 cc. capacity, with walls at least twelve mm. thick, provided with two tubulatures; at the bottom a stop-cock, C, is ground in for regulating the flow of mercury; to the top one is fitted the capillary stem, S, which must be very carefully ground in. These joints are first vaselined, care being taken that none gets inside the apparatus, and cemented in with a sealing wax having nearly the same coefficient of expansion as glass. Metal clamps hold the bulb upon the stand, similar to that for the simple pipette,<sup>1</sup> the weight of the bulb being sufficient to keep it in the lower one; the upper one is provided with screws to hold the neck of the bulb. To render the stem-joint more nearly tight the upper tubulure is made with a mercury seal an inch deep. As thus constructed, the apparatus is



<sup>1</sup> Gill, *Am. Chem. J.*, 14, 231.

absolutely tight at all pressures to which it is likely to be subjected.

Both spark wires were originally fused through the capillary stem, but from the oxides of nitrogen and carbon dioxide formed during the explosions an electrical connection was established sometimes between them and no spark was visible upon turning on the current. To obviate this, one fine spark wire, *w*, is fused through the capillary and the other, *w'*, a platinum wire one and a half mm. in diameter passes through a rubber fitting in the tube carrying the stop-cock up through the mercury to within two mm. of the other. A Mariotte bottle conveniently serves as a reservoir for the mercury and is connected with the pipette by quarter inch "pressure tubing."

It sometimes happens that no spark passes upon closing the circuit. This can be remedied by sucking water into the pipette and expelling it. Upon allowing it to stand all the moisture rises to the top and may be driven out.

The apparatus has been in use for four years, scores of explosions having been made with it. It may be obtained from the Ziegeler Electric Co., Franklin St., Boston.

---

### ESTIMATION OF SULPHUR IN PYRITES.

BY G. LUNGE.

Received June 4, 1895.

IN this Journal Mr. Gladding replies to my remarks on his previous paper on the estimation of sulphur in pyrites. His comments would certainly not give to any reader, who had not my own paper before his eyes, a fair idea of its purport. He states that I admit "that every modification proposed (by Gladding) is accurate in its nature, with one single exception." This conveniently passes over the fact that my "admission" had been saddled with the following addition, for which I had adduced ample experimental proof, "that not in a single case is Gladding's method more correct than mine, and that his modifications cannot be approved, as they greatly lengthen the time required for the analysis, without any corresponding advantage whatever."

In one point, and that just relating to the principal novelty in Gladding's process, I declared him to be entirely *wrong*; viz., in his denial of the fact that it is very easy, by a special kind of washing, to avoid leaving any sulphur in the ferric hydroxide. This point is even more decidedly misrepresented by Gladding (of course, unintentionally) than the others. He says that I "admit that students in my own laboratory have sometimes failed to get out all the sulphur, through imperfect washing." I must really complain of this way of quoting my paper against myself, seeing that I immediately followed up the above by the express statement that such failures occurred in *every* case through having washed in the usual way, instead of the special way prescribed by me for that object; and that the same men have succeeded in every case after their attention had been drawn to this point. That beginners, like those I was speaking of, will make mistakes in most other analytical methods as well, until their attention is drawn to their having neglected some essential precautions, is too patent to be dwelled upon. Nor is it my business to find out why Mr. Gladding and his assistants have failed in a process which succeeds in the hands of *all* beginners in my laboratory, and which is practised by hundreds of chemists, none of whom have ever found any fault with it.

After such an involuntary "admission" of imperfect manipulation on Mr. Gladding's part, it is not possible to take the accuracy of his further results for granted which are contradictory to mine, concerning the differences between our two methods. I repeat that I have afforded in my paper, by a large number of comparative assays, complete proof that (except when the washing was intentionally interrupted before completion) absolutely the same results are obtained by both methods, mine, however, taking considerably less time than his. It seems to me perfectly unnecessary to repeat such proofs, since nothing new can possibly be brought out by it, and I must altogether decline to carry on further discussion with an opponent who treats my paper and work in the above-mentioned style, rewarding my studied fairness by construing it into all sorts of distorted "admissions," and not appreciating the perhaps exaggerated courtesy with which I had explained a decided error in his description of the

decomposing-mixture as being perhaps due to a clerical mistake.

Mr. Gladding seems to have felt that it was necessary to bring heavier metal against me than his own assertions, and he therefore quotes a private communication from Prof. Richards, of Harvard College. He does not mention anything of Prof. Richards having sanctioned the verbatim publication of the "private" communication. For my part, until the contrary is proved, I beg leave to doubt that Prof. Richards would *publicly* have used expressions accusing me of ignorance on a point "which has been known for a number of decades;," *viz.*, the occlusion of barium chloride on the sulphate. Before doing so, he would have looked not merely at my last paper, but also on those I had previously written on the estimation of sulphur in pyrites. He would then have found that I have made researches on this subject for the last fifteen years, and that in my communications the previous work of Fresenius, concerning the difficulty of removing the barium chloride from the sulphate, is referred to as common knowledge. He would then not have misunderstood my last paper as denying that patent fact, which he has so thoroughly investigated in a paper published subsequently to mine. He would have acknowledged that I could not have meant anything else than claiming for my special process the greatest possible approach to truth, which would *not* be attained by preventing all and every occlusion of barium chloride, seeing that the solubility of the barium sulphate in the acid liquid must cause an error in the opposite direction. I am quite sure that Prof. Richards, like every other chemist, is aware of the fact that not one of our analytical separations is mathematically perfect, and that the best analytical methods are those in which unavoidable, but opposite errors are as nearly as possible balanced, and which thus gives a closer approximation to the truth than methods in which one of these errors is eliminated, but the compensating error in the opposite direction is allowed to remain. I have never claimed that the precipitate of barium sulphate obtained according to my method was absolutely devoid of barium chloride, no more than, in the opposite direction, that no barium sulphate whatever remained dissolved in the acid liquor; my claim has been that my method, by compensation of unavoidable errors, gives *correct*

*results.* I need not, however, comment any further upon Prof. Richard's private letter to Mr. Gladding, since everything of importance in this controversy is settled by an authority which Prof. Richards will certainly approve of; *viz.*, a passage in his own paper in the *Zeitschrift für anorganische Chemie*, 1895, 8, 418, which I translate verbatim:

"Moreover the observation is of interest, that the error caused by occlusion ordinarily just about compensates that caused by the solubility of the sulphate, so that the final corrected result is almost the same as the real weight. The average of the uncorrected results is 0.3215 in lieu of 0.3214 gram."

This, I think, disposes of the aid which Mr. Gladding has solicited from Prof. Richards in his attack upon me.

ZURICH, MAY 23, 1895.

## THE PERIODIDES.<sup>1</sup>

BY ALBERT B. PRESCOTT.

Received August 12, 1895.

THE periodides are remarkable as products of extreme additive combination, along with clearly cut crystalline form, distinct physical constants, and instances of rare optical power. They are easily reduced to normal iodides, containing for every atom of iodine firmly bound, one or more iodine atoms loosely bound; therefore they are often and not improperly termed superiodides. Professor Geuther used for them the term polyiodide, perhaps by reason of his view that all their iodine atoms are of equal valence in the molecule.<sup>2</sup> Jörgenson designated them together as superiodides, though including within their structural type certain double polyiodides not understood to contain additive iodine.<sup>3</sup> If these compounds contain, as their behavior has been interpreted to imply, for every atom of iodine that is linked to the base, a number of atoms of iodine linked only to iodine, they offer a striking example of the influence of a basal group upon iodine atoms to which it is not linked. The one iodine atom that is directly united to the nitrogen or other

<sup>1</sup> Read at the meeting of the American Association for the Advancement of Science, Springfield, Aug. 30, 1895.

<sup>2</sup> A. Geuther, 1887: *Ann. Chem.* (Liebig), 240, 82.

<sup>3</sup> M. Jörgenson, 1869: *Ber. d. chem. Ges.*, 2, 465.

base-forming element, by virtue of this union, enables a number of other iodine atoms (say from two to eight) to unite with each other together with itself in an iodine group, capable of forming multiples in polybasal molecules. To this view we are led, possibly misled, by the course of theory. In this relation the molecular weight of free iodine is of interest, and has been studied with care, not only in the vapor<sup>1</sup> but in solutions<sup>2</sup> and in the crystals<sup>3</sup> themselves. The relation to the elemental molecules gives to the periodides an interest greater than that of the mixed superhalides, such as iodoperchlorides and iodoperbromides of bases inorganic and organic. The supersulphides, however, present a corresponding instance of additive combination with a single element, as understood. The organic supersulphides<sup>4</sup> are not so ready of formation or so stable as the organic superiodides, though the reverse seems to be true of the corresponding inorganic super compounds. In its elemental states sulphur surpasses iodine in its unusual capacity for polyatomic molecules. And this comparison holds for the hydrides, as hydrogen pentasulphide was reported in 1888<sup>5</sup>, while hydrogen diiodide, though holding a name in the earlier handbooks<sup>6</sup> is no longer accounted a chemical individual.<sup>7</sup> Again, the superoxides of organic acid radicals were compared with superiodides by Brodie.<sup>8</sup>

To obtain a general survey of the principal known periodides, they may be provisionally classified, chiefly with respect to their bases, as follows :

1. The periodides of potassium and of mercury. Any double metallic polyiodides containing additive iodine and without other acid.

<sup>1</sup> V. Meyer, 1880: *Ber. d. chem. Ges.*, 13, 1010; Neumann, 1880: *Ber. d. chem. Ges.*, 13, 1050.

<sup>2</sup> M. Loeb, 1888: *J. Chem. Soc.*, 53, 805; Paterno and Nasini, 1888: *Ber. d. chem. Ges.*, 21, 2153; Krüss and Thiele, 1894: *Ztschr. anorgan. Chem.*, 7, 52; John Conroy, 1874: *Proc. Roy. Soc.*, 25, 46.

<sup>3</sup> John Conroy, 1876: *Proc. Roy. Soc.*, 25, 51; Compare Geuther, 1887, *Ann. Chem. (Liebig)*, 240, 85.

<sup>4</sup> Palm, 1863: *Phar. Ztschr. Russ.*, 2, 337, 361, 385; A. W. Hofmann, 1868: *Ber. d. chem. Ges.*, 1, 81; E. Schmidt, 1876: *Ann. Chem. (Liebig)*, 180, 287; A. W. Hofmann, again in 1877, *Ber. d. chem. Ges.*, 10, 1087.

<sup>5</sup> Rebs: *Ann. Chem. (Liebig)*, 246, 356.

<sup>6</sup> Gmelin's HandbOOK, 2, 261, 1849, from Baup, *J. Pharm.*, 9, 40.

<sup>7</sup> Gmelin-Kraut's Handbuch, I, 2, 310, 1872.

<sup>8</sup> *J. Chem. Soc.*, 2, 281, 1876.

2. Periodides of ammonium. Periodides of arsonium<sup>1</sup> and of stibonium if they have been obtained. Periodides of the metallic derivatives of ammonium. The same of metallic derivatives of arsonium and of stibonium, if they have been obtained.

3. The periodides of organic bases. They are mostly of the quaternary, and the tertiary<sup>2</sup> bases, of the nitrogen-base family, including bases with oxygen and without it. Phosphonium,<sup>3</sup> arsonium,<sup>4</sup> and probably stibonium<sup>5</sup> periodides are known. And, of another type, that of perhalide of a bare amine base, such as  $(R_3N)I_3$ , at least triethyl phosphine periodide<sup>6</sup> and pyridine periodide<sup>7</sup> have been reported. Also a perhalide taken as pyridine dibromide hydrobromide.<sup>8</sup> The nitrogen-base periodides belong in two categories, (1) those of the alkylammonium bases, and (2) those of pyridine and its derivatives. Polyiodides of the vegetable alkaloids belong in the latter division, except the caffeine and theobromine polyiodides.

4. The periodide of iodonium, the organic iodine base obtained by Victor Meyer last year.<sup>9</sup> The normal iodide of iodonium is of structural interest to polyiodides generally.

5. Aromatic sulphon periodides, as found by Kastle and Hill last year.<sup>10</sup>

6. Acid polyiodides, more or less complex, and double base polyiodides, inorganic and organic, including those in which the iodine is not in additive combination, that is, *not* yielding a distinct part of the iodine to reducing agents with a good end reaction.

<sup>1</sup> Phosphonium normal iodide; Labillardière and Gay Lussac: *Ann. chim. phys.* [2], 6, 304; A. W. Hofmann, 1887; *Ann. Chem.* (Liebig), 103, 355; 1873: *Ber. d. chem. Ges.*, 6, 286. Inflames by contact with iodine.

<sup>2</sup> In Geuther's table, in 1887, of the periodides then known, the only periodides of tertiary bases destitute of oxygen, which appear are a pyridine hydrogen pentiodide, and a quinoline hydrogen tetriodide, both by Dafert (Geuther: *Ann. Chem.* (Liebig), 240, 74). In reporting upon these, in 1883, Dafert says: "Nach den bis jetzt bekannten Thatsachen schientes, dass nur tertiäre und Ammoniumbasen Periodide bilden" (*Monatsh. Chem.*, 4, 510.)

<sup>3</sup> Tetraethylphosphonium triiodide, Jörgensen, *Ann. Chem.* (Liebig), 240, 74.

<sup>4</sup> Tetraalkylarsonium triiodides, Cahours, 1860: *Ann. Chem.* (Liebig), 116, 346; 1862: *Ibid.*, 122, 215.

<sup>5</sup> Jörgensen, 1869: *Ber. d. chem. Ges.*, 2, 463.

<sup>6</sup> Masson and Kirkland, 1889: *J. Chem. Soc.*, 55, 139.

<sup>7</sup> Mr. Trowbridge and the author in another paper of this date.

<sup>8</sup> Grimaux, 1882: *Compt. rend.*, 95, 87; *Bull. Soc. Chim.*, 38, 127.

<sup>9</sup> *Ber. d. chem. Ges.*, 27, 1594, 1894.

<sup>10</sup> *Am. Chem. J.*, 16, 116. A sulphur periodide of another order is that obtained in amorphous condition by Jörgensen, 1869: *Ber. d. chem. Ges.*, 2, 464.

Geuther's classification into triiodides, penta-iodides, hepta-iodides, and enneaiodides, all with one atom of iodine firmly bound,<sup>1</sup> was of service in his own study of structural features. But Geuther admitted a category of sesqui-, di-, tetra-, and hexa-iodides. There is surely a prevailing proportion of *even* numbers of *additive* iodine atoms, making *odd* numbers of *total* atoms of iodine, per "molecule" of the periodide. Generally this is an assumed "molecule" of monobasal proportions. That two or more monovalent groups of the ammonium type should enter into the formation of a periodide molecule, in some cases, is theoretically probable, to say the least, if periodides are individualized in molecules at all. The hypothesis of Jörgenson in 1869,<sup>2</sup> providing for both monammonium and diammonium types of periodides, is not an unreasonable one. Moreover, there is to be considered the probable occurrence of an iodine atom in the fourth position of the organic ammonium group, phosphonium group, etc., with whatever degree of firmness of binding may be determined for it in this position. Take it all in all, therefore, it seems to me that at present we know no law of even or uneven numbers of iodine atoms in superiodides, either to help or to hinder our interpretation of results. With evidence of molecular weight we may gain approach to such a law.

In division 6 of the classification above there are without doubt included certain strictly normal iodides. The iodomercurates as strongly marked double iodides, and the Herapathites as representative acid superiodides come in this division. An interest in the iodomercurates of the nitrogenous bases<sup>3</sup> has been but one among several causes contributing to my own interest in this subject at present. But I have not yet made such an inquiry into the action of deiodinizing agents upon the known double iodides as might reveal what superiodides there are among them. Some of the tabulations of the super-iodine in double inorganic polyiodides given by Geuther<sup>4</sup> seem to invite further inquiry. The acid periodides in many cases undenia-

<sup>1</sup> *Ann. Chem.* (Liebig), 240, 74, 80, 1894.

<sup>2</sup> *Ber. d. chem. Ges.*, 2, 465, 1869.

<sup>3</sup> *Am. Chem. J.*, 14, 607, 1892; 2, 294, 1880. *Pharm. Rund.*, 12, 146.

<sup>4</sup> *Ann. Chem.* (Liebig), 240, 81.



bly contain additive iodine, but the question of their constitution, like that of mixed halides in general<sup>1</sup> is more complicated and is perhaps of less special significance, than that of the simple polyiodides.

With the exception, then, of the metallic, the iodonium and the sulphon periodides, the formation of superiodides is limited, so far as I have found, to compounds of the nitrogen family of elements.

The first periodide recognized, so far as I find record, may have been that of ammonium, termed by Berzelius the biniodide. After the discovery of iodine the first workers upon the alkaloids seem to have mistaken, in some instances, a produced periodide for a mixed excess of iodine to be taken up by more alkaloid in preparation of the hydriodides.<sup>2</sup> In 1839 Bouchardat,<sup>3</sup> a medical writer in Paris, recounts that, when dogs were being surreptitiously poisoned with strychnine in Paris, and an antidote was asked for, first Guibourt recommended powdered galls, and then Donné advised iodine tincture,<sup>4</sup> whereupon Bouchardat himself, approving the use of iodine, said they should use it in potassium iodide solution. He then set forth some interesting characters of the alkaloid periodides, comparing them with ammonium periodide, quoting for this the name from Berzelius mentioned above. De Vrij has said that Bouchardat anticipated Herapath in production of iodosulphates. A modest memoir of Donné, in connection with the Parisian interest just referred to, upon the use of iodine as an analytical reagent for vegetable bases, was referred for criticism to D'Arcet and Chevreul, who made quite an elaborate report<sup>5</sup> upon the action of free chlorine, bromine, and iodine, in intensive application, with admonition as to undue dependence upon any single analytical reactions. In 1846, in his summary of the distinguishing reactions of the more important

<sup>1</sup> The Chloriodides of Organic Bases, and Pyridine Chloriodide, Pictet and Krafft, 1892: *Bull. Soc. Chim.* [3], 7, 72.

<sup>2</sup> Pelletier and Caventon, 1819. *Ann. chim. phys.* [2] 10, 142; *Ann. der Phys. Gilbert*, 63, 306.

<sup>3</sup> Bouchardat, 1839: *Compt. rend.* 9, 475; *L'Institut*, 7, 358.

<sup>4</sup> Both apparently acting under the opinion, due to that little chemistry which has often brought all chemistry into disrepute, that a precipitant in a test-glass will serve as an antidote in the stomach.

<sup>5</sup> *Ann. chim. phys.* [2] 38, 82.

alkaloids,<sup>1</sup> v. Planta-Richenau specifies for each a precipitation by free iodine. In 1854, shortly after A. W. Hofmann's famous elucidation of organic ammonium bases,<sup>2</sup> Weltzien contributed a full and careful description<sup>3</sup> of the tetramethyl and tetraethyl ammonium triiodides. In 1858 Müller added a good account<sup>4</sup> of quaternary mixed alkyl ammonium triiodides. In 1866 Wagner<sup>5</sup> proposed iodine precipitation and a method of treatment of the periodide precipitates for separation of alkaloids from extractive matters. And Tilden made a contribution in 1866.<sup>6</sup>

The masterly work of Jörgensen, beginning with his dissertation at Copenhagen in 1869, continuing for about nine years<sup>7</sup> in this field, and extending over nearly all relations of polyiodides in general, have had the respect of all chemists, while hardly yet fully assimilated.

In 1887 this subject was taken up by Professor A. Geuther, at Jena, who contributed<sup>8</sup> a good number of new periodides from his own laboratory, with a tabulation of all then obtained, and a vigorous and independent study of the features of structure. The crystallographic investigations were made by Prof. Lüdecke. Prof. Geuther died in 1889.

In 1869 Jörgensen<sup>9</sup> formulated his idea of the probable structure of "these compounds," taking iodine as trivalent, as follows:<sup>10</sup>

$R_4N \cdot I : \begin{smallmatrix} I \\ \vdots \\ I \end{smallmatrix} ; R_4N \cdot I : \begin{smallmatrix} I & I \\ \vdots & \vdots \\ I & I \end{smallmatrix} ; \text{etc., for periodides of uneven numbers of iodine atoms.}$

$R_4N \cdot I : \begin{smallmatrix} I & I & I \\ \vdots & \vdots & \vdots \\ I & I & I \end{smallmatrix} : I \cdot NR_4$  for those of even iodine numbers.

And  $R_4N \cdot I : \begin{smallmatrix} I \\ \vdots \\ I \end{smallmatrix} : Hg$  for a typical iodomercurate. This simple

<sup>1</sup> Heidelberg dissertation, 1846. *Ann. Chem. Pharm.*, 74, 245.

<sup>2</sup> 1850-51: *Phil. Trans.* I. 93-131, 357-398.

<sup>3</sup> *Ann. Chem. Pharm.*, 91, 33; 99, 1.

<sup>4</sup> *Ann. Chem. Pharm.*, 108, 1.

<sup>5</sup> *Ztschr. anal. Chem.*, 4, 387.

<sup>6</sup> *J. Chem. Soc.*, 19, 145, 1871.

<sup>7</sup> *J. prakt. Chem.*, 1870-78, [2] 2, 347, 433; 3, 145, 328; 14, 213, 356; 15, 65, 418; 16, 352. *Ber. d. chem. Ges.*, 2, 460, 1869.

<sup>8</sup> *Ann. Chem. (Liebig)*, 240, 66-91.

<sup>9</sup> *Ber. d. chem. Ges.*, 2, 465, 1869.

<sup>10</sup> The present writer gives  $R_4N$  as an expression for any organic base of nitrogen, instead of "Alk" used by Jörgensen.

conception is, of course, consistent with an iodine valence of five or of seven.

Geuther<sup>1</sup> drew from the optical studies of the color of iodine crystals by Conroy the indication that the molecular mass of the crystalline element is that of  $(I_2)_n$ . He made this generalization as to color of the periodides, that the tri and hepta iodides were red-brown to violet-blue, and the penta- and enneaiodides green to green-black, the higher iodine numbers giving the deeper shades.<sup>2</sup> He presents structural schemes of orders as follows :

For the triiodides,  $(R_3I_3)I_3 = 6(RI.I_3)$ ; for the haptaiodides,  $(R_3I_2)I_3 = 2(RI.I_3)$ ; for the pentaiodides,  $(R_3I_4)I_3 = 4(RI.I_3)$ ; and for the enneaiodides,  $(R_3I_5)I_3 = 2(RI.I_3)$ .

In the laboratory of the writer the preparation of periodides of pyridine is in the hands of Mr. P. F. Trowbridge, and an account of some of these is communicated by both of us in another paper, while he continues the work for pyridine and quinoline. Some work on periodides of the more simple of the aliphatic bases is in other hands. In this subject a pyridine normal polybromide, namely a trimethylene bromide, obtained by Mr. R. F. Flinterman, is reported upon in a paper by him and myself. Therewith it is desired to continue studies of the limit of tertiary base addition to halogen alkyls which are secondary and tertiary. I submit also a note with the observations of several workers upon the preparation and properties of a few pyridine alkyl normal iodides, and Mr. S. H. Baer has some work in progress with me upon pyridine alkyl hydroxides.

ANN ARBOR, MICHIGAN.

## AN IMPROVED GAS REGULATOR.

BY F. P. DUNNINGTON.

Received August 7, 1895.

SOME years ago I published<sup>2</sup> a description of a gas-regulator, which is now so modified as to make it less bulky and more reliable. Its arrangement may be understood by reference to the

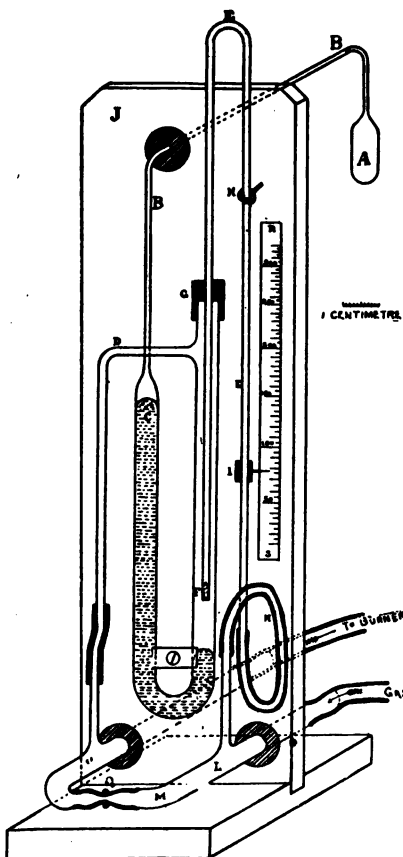
<sup>1</sup> *Ann. Chem.* (Liebig), 240, 85.

<sup>2</sup> This generalization, to which Prof. Geuther acknowledged reported exceptions, finds little support in the observations which Mr. Trowbridge and the writer have been able to make.

<sup>3</sup> *Am. Chem. J.*, 4, 2.

figure, with the accompanying scale the measure of the inner walls of the tubes may be ascertained, and other dimensions are drawn to two-thirds of this scale.

The tube B with stout walls, about forty cm. long is attached to the bulb A. Into the tube C, thirty-five cm. the small side tube D is fused. Unite C to B, and bend all as indicated. Into the tube L, fuse the side tube and at M, bend at right-angles; similarly make the tube O. These latter are passed through corks, set in the upright board J. B also is passed through this board, which then serves to screen the apparatus from the heat of the bath, and C is firmly fastened to it.



The light tube E, fifty cm. long terminates at F with a slit, made by blowing a hole through its side and then drawing it out. This slides through a joint at G, made with two sections of rubber tubing, and also through a screw-eye at H. Upon E slides a bit of rubber tubing I, which is compressed by a wire around it, the end of which serves as an index. E is connected to L by

fifteen cm. of light one-eighth rubber tubing, D is connected with O, and L is joined to O by a rubber tube pinched by a screw clamp at Q. A piece of card-board, RS, is pasted to the board. By warming and cooling the tube C is filled with mercury, as indicated. To graduate the apparatus, connect L with gas supply and O with a burner, pinch the tube at N, open Q sufficiently

to maintain a small flame, relieve N and push down E until the flow of gas through F just ceases; then slide the index I almost to the lower end of E, and upon the paper mark the point corresponding to the temperature of the bulb A. Place bulb A and a thermometer in a water-bath, with the burner beneath, and raise E. When the temperature of the bulb A is, say  $50^{\circ}\text{C}$ , lower E until the flow of gas through F just ceases, and make a mark on the scale for  $50^{\circ}$ , similarly fill out this scale to  $100^{\circ}\text{C}$ ., and for higher temperatures employ an air-bath, or preferably a paraffin bath.

In using the apparatus, E is lowered until the gas through F is just cut off and the index is moved up or down the tube until it points to the figure marking the temperature of the atmosphere in which A is exposed. Having fixed the index, the tube E is raised until the index marks the temperature at which it is desired to maintain the bulb.

This adjustment of the index, whenever the regulator is used, eliminates the effect of the thermometer and barometric pressure upon the volume of air confined in A, B and C, and so corrects a defect existing in most instruments of this kind.

UNIVERSITY OF VIRGINIA.

---

## INSPECTION OF COTTON FOR USE IN THE MANUFACTURE OF GUNCOTTON.<sup>1</sup>

BY CHARLES E. MUNROE.

Received August 2, 1895.

WHEN converting cotton into guncotton by immersion in mixed acids, as practiced in the Abel process, it is essential that the cotton should rapidly absorb the acid for if the portion that is taken for immersion be but slowly absorbent, it is likely when but partly saturated to rise to the surface of the acid and on exposure to undergo the rapid decomposition technically called "firing." To secure the desired result the cotton should be free from oil, grease, and any protecting body. Their presence not only diminishes the absorptive power of the cotton but they, in common with the knots, tangles, cops, hulls, seeds, or similar foreign bodies, promote decomposition. It is a common practice to

<sup>1</sup> Read at the Brooklyn meeting.

use weaver's waste, or waste from the cotton gauze factories, in this manufacture on account of its cheapness and because it is found also that the thready form permits of ready handling in the hand-dipping and its compactness diminishes the amount of air which becomes entangled in the mass, as compared with that entangled in a similar mass of cotton "in the wool," and consequently the bouyancy of the mass is less.

Such waste necessarily becomes soiled with oil or grease, to a greater or less degree, during the carding and spinning, and it may contain besides knots, cops, tangles, and foreign bodies of various kinds, which latter are removed by means of the picker, while the oil and grease are removed by boiling with soda lye. Hence in determining the relative value of various samples of cotton offered for purchase, the relative amount of the grease, foreign bodies, and waste to be removed and of knots and tangles present, together with the general cleanliness of the sample, are to be considered.

Based on considerations such as these, the method of inspection is as follows :

1. Optical examination for color, cleanliness, presence of cops, knots, tangles, and foreign bodies, and for relative length and strength of fiber.

2. Odor.

3. Moisture, which is determined by drying a portion at 100° C. to constant weight.

4. Ether extract, which is determined by subjecting the weighed sample to the action of petroleum ether (boiling-point 50°-80° C.) in a Soxhlet extractor until the sample ceases to lose weight. The method of procedure is to expose the weighed sample in a light glass basket to ten automatic exhaustions, when it is removed, dried, and weighed. It is then returned to the extractor and subjected to five automatic exhaustions, when it is again dried and weighed. If it has lost weight by the last treatment the basket and contents are again returned to the extractor and exhausted three times and this treatment is repeated until the weight becomes constant.

The weight of the samples taken in the experiment varied between one and one and a half grams and the extractor had a

capacity of forty cc. for each automatic exhaustion. The ether extracts the oily matters in the cotton, both those which occur naturally and those which it has absorbed in the processes to which it has been subjected.

5. Soda-lye extract, which is determined by boiling the weighed sample for eight hours in a solution of sodium hydroxide of the same strength and in the same proportions as that used in the factory in the first boiling tub. For this purpose the waste, if in long bundles, is cut into pieces about one inch long, and ten grams of it placed in a beaker of about a half liter capacity, 104 cc. of a solution of caustic soda containing 17.305 grams to the liter (thirty-five pounds to 250 gallons of water) are poured upon it and the boiling carried on for eight hours, fresh water being added from time to time to keep the solution at constant volume. At the end of eight hours the liquid is poured off and the sample placed in a cotton filter, where it is squeezed and washed with hot water until the wash water gives no alkaline reaction. The sample is then dried to constant weight.

6. Ash, which is determined by placing from one to one and a half grams of the sample in a weighed platinum crucible pouring melted paraffin upon the mass, igniting it from the top, allowing it to burn slowly until the flame dies out and then igniting the residue to constant weight.

7. Rate of absorption of water. In making this test a sample of the material is thrown or dropped lightly on the surface of distilled water and the time between when it touched the surface and when (through absorption of the water by capillarity) it sinks to the bottom noted. One of the requisites for cotton suitable for making smokeless powder is that it shall sink in two minutes. In these experiments the cottons were tested not only in the condition in which they were received but also after treatment with ether; after drying for moisture, and after boiling with soda-lye; all being in the dry state. The vessel used varied in diameter from three to six inches, while the temperature of the water varied from 20° to 25° C. These differences or that of the size and form of the pellet seemed to produce no effect, but special attention must be paid to having distilled

water with a perfectly clean surface. With the same sample of cotton there were considerable variations in the time of sinking to the bottom of the vessel although the time of becoming thoroughly saturated so as to become submerged at the surface was fairly constant. The fact that the mass remained at the surface after saturation was found usually to be due to a bubble of air entangled in the mass which bouyed it up, or, less often, to a small portion of the mass being non-absorbent. This condition was evident on inspection as the non-absorbent portion of the sample remained opaque, while the absorbent portion appeared translucent. When the absorption failed to begin at once it usually did not take place at all, even after twenty-four to forty-eight hours exposure, or even when the whole mass was forcibly plunged beneath the water, in fact in these cases there seemed to be an actual repulsion between the water and the fiber. As what we seek to learn by this test is the relative rates at which the cottons tested will suck up the mixed acids during dripping, it would seem sufficient to note the moment at which they become thoroughly wet and submerged beneath the surface.

The detailed results obtained with five samples submitted at one time are as follows:

1. *Sample 1.*—Off white, yellowish tint. Cop waste. No cops in sample. No knots. Long threads, somewhat tangled. Free from dirt and rust spots. Strong fiber.

*Sample 2.*—Off white, yellowish tint. Cop waste. No cops in sample. No knots. Long threads, somewhat tangled. Free from dirt. Very strong fiber.

*Sample 3.*—Off white, yellowish tint. Long threads, freer from tangles than 1 or 2. Free from dirt. Strong fiber.

*Sample 4.*—White. Partly short threads and partly loose fiber as if picked. Has evidently undergone special treatment. No cops, knots, tangles or dirt, but a few rust spots.

*Sample 5.*—White. Whole fibrous and wooly, as if picked, the fibers being not over an eighth of an inch in length. Has evidently undergone special treatment. No cops, knots, tangles or dirt, but a few dark specks.



2. *Sample 1*.—Faint odor of oil.  
 “ 2.—Very faint odor of oil.  
 “ 3.—Marked odor of oil.  
 “ 4.—Very faint odor of oil.  
 “ 5.—Very faint odor of naphtha (?)

The percentages of moisture, ether extract, soda-lye extract, and ash, (3, 4, 5, and 6) are given in the following table:

Sample No.	Moisture.	Ether extract.	Soda-lye extract.	Soda-lye extract less moisture and ether extract.	Ash.
1.	4.93	0.97	9.16	3.26	0.86
2.	4.79	0.49	10.36	5.08	0.75
3.	5.17	1.20	9.26	2.80	0.80
4.	4.36	0.53	13.69	8.80	0.61
5.	4.69	0.09	7.58	2.80	0.40

7. The rates of absorption of water found was as follows:

Sample No.	Original condition of sample.		After exhaustion with petroleum ether.		After boiling in soda-lye.		After drying for moisture determination.	
	Min.	Sec.	Min.	Sec.	Min.	Sec.	Min.	Sec.
1.	∞		∞		{ 2 00 1 00 2 00		∞	
2.	∞		∞		{ 2 00 1 00 1 40 50 3 30		∞	
3.	∞		∞		∞		∞	
4.	{ 3 15 5 15 1 15		{ 60 45		{ 10 8 7 4		{ 3 00 4 00 7 45	
5.	∞		{ 45 45 20 43		{ 10 4 4		∞	

∞ No submersion after twenty-four hours' exposure.

The appearance of the ash and of the soda-lye after extraction are worthy of notice. In samples 1, 2, and 3, the ash obtained was of a light green color, the green portion being soluble in water, leaving a yellowish residue, which was insoluble. The ash of samples 4 and 5 was reddish. The color seemed to be due,

in each case, to iron, it being in the ferrous condition in the first three cases and the ferric in the last two. As the latter evidently have been bleached with chlorine, this treatment would naturally oxidize the iron.

Soon after boiling the lye with the cotton began, the former, which was colorless at the start, began to acquire a color which increased in intensity for some hours. In the case of samples 1, 2, and 3, the lye, when the operation was finished, was of a pale sherry wine color, No. 4 was of a port wine color, while No. 5 was of a deep sherry wine color.

From this examination the samples are divided into two classes, *viz.*: cop waste and short fiber, treated cotton. Samples 1, 2, and 3 being in the first class and samples 4 and 5 in the second.

The short-fibered cotton cannot be nitrated successfully with the usual appliances and the presence of chlorine is objectionable as the cellulose nitrates produced from such cotton cannot be washed neutral.

Of the cop wastes, which are adapted to our present methods of manufacture, sample 1 seems on the whole to be the best, though it is but little superior to sample 2.

From the observations made it was found that in eighteen samples of cotton waste—

The moisture varied from 3.38 to 8.40 per cent.

The ether extract from 0.00 to 7.10 per cent.

The soda-lye extract from 3.53 to 5.36 per cent.

The ash from 0.05 to 1.79 per cent.

The rate of absorption after soda-lye extraction from one second to over twenty-four hours.

A sample of cottonseed lint gave—

Moisture.	Ether extract.	Soda-lye extract.	Ash.	Rate of absorption.
6.16	2.35	28.54	4.83	∞

A sample of waste cotton gauze gave—

Moisture.	Ether extract.	Soda-lye extract.	Ash.	Rate of absorption.
7.37	0.50	3.89	.95	7 seconds.

The rates of absorption quoted are for samples dried after receiving the soda-lye treatment. As indicated above, observations were also made on the original sample and after treatment

with ether, both after drying. The highest rate was obtained after boiling with soda-lye; many samples being still non-absorbent after treatment with ether.

Treatment with the soda-lye even improved the absorbent power of the samples of "Absorbent Cotton" submitted for testing the rate being increased from three seconds for the dried, untreated cotton, to one second for that which had been treated.

Experiments were made on the absorptive capacity of the cotton, and in one case a six-gram sample of absorbent cotton was found to retain ninety-three grams of water or 15.5 times its own weight.

---

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY  
No. 8.]

### REDUCTION WITH MAGNESIUM AMALGAM.

BY HERMANN FLECK AND LEWIS L. BASSETT.

Received August 21, 1895.

THE subject of neutral reducing agents has been taken up in a recent publication by J. B. Cohen and R. Ormandy.<sup>1</sup> The study of the same subject has been carried on in this laboratory during the past year. For this purpose magnesium amalgam, two per cent., was prepared in the following manner:

The required amount of mercury is placed in a small Hessian crucible and half covered with magnesium powder. The lid is put on loosely and the blast applied until a loud hissing noise begins. Once begun the reaction takes place by itself. This is repeated until the requisite quantity of magnesium powder has been added. A more uniform mass is obtained by boiling mercury in a hard glass tube, open at one end; then adding the magnesium in small quantities and shaking vigorously after each addition. The product is a silver white, crystalline, pasty mass which decomposes water with great energy and evolution of heat, and which upon exposure to air becomes covered with a black mass; probably a lower oxide of magnesium.

#### MAGNESIUM AMALGAM AND HYDROCYANIC ACID.

Two hundred cc. of ninety-six per cent. alcoholic solution of hydrocyanic acid containing eight grams of the acid were placed

<sup>1</sup> *Ber. d. chem. Ges.*, 27, 1505.

in a liter distilling bulb connected to a condenser by a rubber tube. The condenser, by means of a long glass tube, led into a flask containing dilute hydrochloric acid, and this in turn was attached to a suction pump. After cooling in a mixture of ice and salt a small quantity of the amalgam was introduced into the neck of the distilling bulb, the cork replaced, and by a sharp jerk introduced into the liquid. When the theoretical amount of two per cent. amalgam had been introduced the contents were directly distilled into dilute hydrochloric acid evaporated to dryness, redistilled with addition of caustic soda into dilute hydrochloric acid, evaporated to dryness, and extracted with absolute alcohol. A small amount of ammonium chloride remained, produced by the action of hydrochloric acid upon the unconverted hydrocyanic acid.

The yield was fifteen per cent. 0.1122 grams methylamine platinichloride gave 41.08 per cent. platinum, the theory being 41.24 per cent. With more than the theoretical amount of amalgam a larger yield can surely be obtained.

#### MAGNESIUM AMALGAM AND BENZONITRILE.

Ten grams benzonitrile were dissolved in 200 cc. of ninety-six per cent. alcohol and twice the theoretical amount of amalgam added under the same conditions as above. The reaction product was filtered on a suction pump from the magnesium hydroxide formed and evaporated to dryness with hydrochloric acid, caustic soda added and extracted three times with ether. The ethereal solution was evaporated with hydrochloric acid to dryness and the residue extracted with absolute alcohol. There remained one gram of a crystalline substance melting under  $100^{\circ}\text{C}.$ , whose alcoholic solution immediately reduced platinic chloride. This substance, possibly of a hydride nature, will be further investigated.

#### MAGNESIUM AMALGAM AND ACETOPHENONE.

Ten grams acetophenone were dissolved in fifty cc. ether and somewhat more than the theoretical quantity of amalgam added. When the mass cakes, alcohol is added and then sufficient water to completely decompose the amalgam. Dilute hydrochloric acid is added to dissolve the magnesium hydroxide formed, and

the semi-crystalline mass extracted with ether, the ethereal solution evaporated to dryness, crystals formed freed from oily substance by washing with ligroin, and recrystallized from benzene.

Of the products theoretically possible, acetophenone pinacone, or diphenyl dimethyl glycol, forms large colorless prisms, melting at  $120^{\circ}$  C. The product obtained melts at  $120^{\circ}$  C., and in every particular corresponds to the above. The yield was excellent.

It is our intention to further pursue the investigations with nitriles, ketones, oxynitriles, and amido-nitriles.

UNIVERSITY OF PENNSYLVANIA.

## TWO DEFINITE CARBIDES OF IRON WITH CHROMIUM (MOLYBDENUM AND TUNGSTEN).

BY JAMES S. DE BENNEVILLE

Received September 6, 1895.

A PREVIOUS paper<sup>1</sup> described in detail the results of a chemical examination of some ternary alloys of iron with chromium, molybdenum, and tungsten. In the course of the experiments there described two definite carbides were separated and it is proposed to give additional details obtained later. The physical description of the crystals is taken from Professor F. Lynwood Garrison's discussion of the paper cited.<sup>2</sup> The alloys described were made by taking pairs of the elements: tungsten chromium irons, molybdenum chromium irons, and molybdenum tungsten irons. The proportions taken were not based on equal weights but on quantities taken in the ratio of the atomic masses of the constituents. They were 1:1, 5:1, and 1:5. A lump of cast iron weighing fifty grams was imbedded in the mixture and melted, a white heat being maintained for an hour. The aggregations to be described were found in the chromium alloys and only in the two alloys (Nos. II and V) in which chromium was the predominant metal. These two alloys showed well individualized crystals differing in form and reactions from the matrix in which they were imbedded.

<sup>1</sup> Iron and Steel Institute, May meeting, 1895.

<sup>2</sup> *Ibid.* I take this opportunity of expressing my indebtedness to Professor Garrison, through whose kind offer I was enabled to present this paper to the council of the Institute.

Berthier and also Percy<sup>1</sup> have noted the presence of needle-shaped crystals in ferrochromium and in chromium steels. Further details are not given. Behrens and Van Linge, in a recent paper, have described at length the physical and chemical properties of segregations in ferrochromium. On treating the alloy with acid they obtained bayonet or rod-shaped crystals, three to four millimeters in length, a few being eight to ten, non-magnetic, of hardness 7.5. The composition, however, varied with the ferrochromium from which they were obtained; ferrochromium with 13.8 per cent. chromium, eighty-one per cent. iron, and five and one-half per cent. carbon, giving the compound  $\text{Cr}_2\text{Fe}_3\text{C}_4$ , whereas with fifty per cent. chromium, the composition was approximately  $\text{Cr}_2\text{FeC}_2$ . They point out the relation of the first compound to  $\text{Fe}_3\text{C}$ , chromium replacing a part of the iron, and consider that chromium forms "double carbides less soluble in iron than the ferrocabides, at the same time facilitating the crystallization of the latter."<sup>2</sup>

Considering the marked development of the segregations in the ternary alloys it appears to me doubtful whether they are to be referred, as to origin, to the iron carbides. The prismatic form is not a dominant one with the iron carbides, although it is found under certain conditions. Howe, citing Sorby, notes three successive crystallizations in hard cast-steel. I quote him in *extenso*: he says, "First we have the large prismatic columnar crystals, normal to the cooling surface, and conspicuous on fracture. They apparently represent the first crystallization, be it of hardenite, be it of the hypothetical mother-of-pearlyte, which in this case has expelled the excess of cementite present, distributing it as an elongated meshwork between the crystals. Secondly, these columns or crystals are chiefly composed of groups of pearlyte, disposed with little or no relation to the columnar structure, indeed shooting from one column into another, and apparently formed from the substance of the primary crystals of a second crystallization. Finally, by a third crystallization, each of the individual members of the radial

<sup>1</sup> Percy, *Iron and Steel*, p. 186. Berthier from Percy not the original.

<sup>2</sup> *Recul trav. chim. Pays-Bas.*, 13, 155-181. From the abstracts in *J. Soc. Chem. Ind.*, 14, 275, 1895, and *J. Chem. Soc.*, 64, 452, 1896.

groups of pearlyte has split into parallel layers of cementite and ferrite, which apparently occupy the space previously occupied by a simple undivided crystal." Again, "the exterior columnar structure is clearly due to the rapid escape of heat from the shell of the ingot into the mold. We may suppose that the metal naturally tends to crystallize in equiaxed grains: that there is a struggle between this tendency and the tendency to crystallize in indefinitely long prisms which the rapid cooling sets up. As the walls thicken and the flow of heat outward slackens, the prismatic tendency weakens: the sudden transition from the prismatic to the equiaxed formation suggests that no resultant, no compromise is possible, so that from the moment when the equiaxial tendency outweighs the prismatic it reigns alone, as if its rival were not."<sup>1</sup> This is the only mention of prismatic structure in ordinary carbon steel that I find in the "Metallurgy." If the intense hardness of ferrochromium, ferrotungsten, and ferromolybdenum is to be ascribed to the conversion of the carbon present into hardening carbon and its retention in that form—although from the researches of Riche and especially of Moissan this hardness can just as well be attributed to carbides of chromium, tungsten, or molybdenum—the alloys under discussion can be justly compared to hard cast-steel containing a large excess of carbon and the prismatic form of the crystals in II and V could be attributed to a structure found in such steel as described above. However, the conditions are by no means identical. The crystals in II and V are present throughout the mass forming a network with the interstices filled in by the equiaxial granular material. There is no line where the equiaxial tendency has overcome the prismatic and so sharply differentiated the alloys into an external prismatic shell surrounding an interior of equiaxed grains. Also, the crystals show a marked increase in density as compared with the granular material and the alloys in which they are found differ in hardness from the rest of the series. In fact, the crystals give every evidence from their sharpness of outline of having a higher freezing-point and as having separated out from the mass of the alloy at a time when it was not liquid enough to effect their

<sup>1</sup> Metallurgy of Steel, p. 182, 183.

segregation into any one portion of the alloy, but liquid enough to secure their own crystalline form at the expense of compounds crystallizing later. For when a mass of iron is allowed to cool uniformly, from the resultant structure it would appear that the constituent compounds have freezing points not so far removed from each other as to effect the segregation of any one of them into a part of the mass. This has no reference to the microstructure of iron and steel in which the compounds identified appear to be somewhat unstable in nature, passing readily from one form to the other even by cold working. The columnar structure is only stable under the limited conditions existing for its formation and by slight alteration of the method of cooling or of working passes readily into other forms. Also, the columns are often distinctly a mere structural arrangement of the granular material with radial lines forming prismatic aggregations in which the granular components are distinctly manifest. There is in the micro structure of steel a compound to the development of which might be attributed the prismatic and needle-like form when found in iron alloys. This has been described by Osmond<sup>1</sup> and named by him martensite. It is found in steel of 0.45 carbon heated to 825° and tempered at 720° in a cooling mixture of -20°. It occurs "in groups of needles or rather of rectilinear fibers lying parallel and separated or not by a granular or vermicular filling." From the grouping of three systems of fibers respectively parallel to the three sides of a triangle he regards them as crystallites of the cubical system. In the absence of any other source the form of the prismatic needles found in ferrochromium and in tungsten chromium irons (II) and molybdenum chromium irons (V) could be attributed to the development of the microstructural element, to the fixation of the prismatic columnar structure, or to the rod-shaped fiber structure of Abel's carbide  $\text{Fe}_3\text{C}$ . As to the two first, in despite of their instability and the absence of any boundary line between the prismatic and granular formations, it seems to me better to attribute the form to the carbide of chromium isolated by Henri Moissan.<sup>2</sup> This carbide, of formula  $\text{CCr}_3$ , he describes

<sup>1</sup> Bull. de la. Soc. d'Enc. pour. l'Ind. Nat., May, 1895.

<sup>2</sup> Bull. Soc. Chim. Paris, 11, 1016, 1894.



as forming needles one to two cm. in length lining the cavities found in the melt. He also isolated a carbide  $C_2Cr$ , occurring in brilliant lamellae. Of the two the lamellar carbide was the harder, scratching topaz but not corundum, whereas the prismatic carbide scratched glass readily, but quartz only with difficulty. Both carbides were very stable compounds and were chemically inert. The crystals found in the ternary alloys were confined to the high chromium compounds in which the ratio of chromium to tungsten or molybdenum was as five to one. The alloys, II and V, were much softer than the other alloys, which would be the case if hardness is dependent on the carbide of chromium present. For comparison, Table I gives the composition of the series of alloys.

If now the prismatic segregations in ferrochromium be compared it will be found that, with the exception of the compound  $Fe,Cr,C_2$ , chromium is the dominant constituent in the carbide. For example :

TABLE II. SEGREGATIONS IN FERROCHROMIUMS.

	B. and Van L. $Fe,Cr_2C_3$	B. and Van L. $FeCr_2C_3$	V. Analysis 1 $Fe(CrMo)_5C_4$	V. Analysis 2. $Fe(CrMo)_5C_4$	II. $Fe(CrW)_5C_4$	II B. $Fe(CrW)_5C_4$
Iron .....	0.8100	0.3030	0.4639	0.4650	0.4724	0.4723
Chromium ..	0.1380	0.5671	0.4623	0.4606	0.3542	0.3682
Molybdenum ....	....	....	0.0201	0.0194	....	....
Tungsten ...	....	....	....	....	0.1139	0.1007
Carbon .....	0.0550	0.1299	0.0553	0.0559	0.0595	0.0599

$Fe,Cr,C_2$ , on the contrary, could fairly be classed as derived from an iron compound— $Fe_2C$ . This compound, isolated by Abel and subsequently by Muller, is described as a dark-grey residue; Osmond and Werth obtained it in the form of bright plates; Behrens and Van Linge treating Dannemora iron, obtained it as bright spangles and rods; and Arnold and Read obtained it in two forms, as bright silver plates and as a grey black powder in microscopic granules.<sup>1</sup> The segregations in the ternary alloys are to be compared with the "brilliant white radial needles" described by Behrens and Van Linge and which

<sup>1</sup> Abel—Proc. Inst. Mech. Eng., 1895, p. 30; Muller—Stahl und Eisen, No. 5; Osmond and Werth—Annales des Mines 1895; Behrens and Van Linge—as cited, 1894; Arnold and Read—J. Chem. Soc. Trans., 65-788, 1894. Also Ledebur Jour. Iron and Steel, Inst. 1893, II. 53. The quotations following are from the abstract of Behrens and Van Linge's paper.

TABLE I. COMPOSITION OF THE ALLOYS. *J. Iron and Steel Institute*, I, 1895.

ALLOY	I	II	III	IV	V	VI
Total carbon.....	0.0317	0.0299	0.0311	0.0323	0.0312	0.0323
Carbon evolved by hydrochloric acid.....	0.0122	0.0074	0.0127	0.0104	0.0084	0.0130
Carbon in hydrochloric acid residue.....	0.0195	0.0225	0.0184	0.0219	0.0228	0.0193
Carbon in nitric acid residue.....	none	Table VIII	none	none	Table VIII	none
Silicon evolved by hydrochloric acid.....	0.0033	0.0142	0.0072	0.0075	0.0055	0.0022
Silicon in hydrochloric acid residue.....	0.0193	0.0193	0.0130	0.0103	0.0119	0.0051
Phosphorus evolved by hydrochloric acid.....	0.0019	0.0025	0.0012	0.0014	0.0020	0.0003
Phosphorus in hydrochloric acid residue.....	0.0009	0.0007	0.0003	0.0006	0.0005	0.0020
Manganese.....	0.0004	0.0043	0.0049	0.0013	0.0027	0.0004
Sulphur.....	—	—	.....	.....	.....	.....
Chromium.....	0.0846	0.1207	0.0211	0.0802	0.2257	0.0485
Tungsten.....	0.3382	0.0440	0.2125	.....	.....	.....
Molybdenum.....	—	.....	.....	0.1184	0.0735	0.3065
Iron.....	0.5197 D	0.7754 D	0.7087 D	0.7531	0.6470 D	0.5999
Specific gravity.....	11.010	7.995	10.257	7.571	7.300	8.410
Formula.....	$\text{Fe}_{46}\text{Cr}_7\text{W}_9$	$\text{Fe}_{33}\text{Cr}_{19}\text{W}$	$\text{Fe}_{34}\text{Cr}_7\text{W}_9$	$\text{Fe}_{44}\text{Cr}_{16}\text{Mo}_9$	$\text{Fe}_{48}\text{Cr}_{18}\text{Mo}_4$	$\text{Fe}_{50}\text{Cr}_{17}\text{Mo}_7$
Condensation from composition difference.....	2.951+	0.453+	1.869+	0.089+	0.054—	0.965+

ALLOY	VII	VIII	IX	Cast Iron used.	Chromium for steel.	Tungsten for steel.
Total carbon.....	0.0335	0.0289	0.0290	0.0331	0.0773	0.0343
Carbon evolved by hydrochloric acid.....	0.0162	0.0126	0.0147	0.0039	.....	0.0014
Carbon in hydrochloric acid residue.....	.....	.....	.....	0.0292	.....	.....
Carbon in nitric acid residue.....	none	1.0163	0.0153	0.0286	.....	.....
Silicon evolved by hydrochloric acid.....	0.0073	0.0184	0.0023	0.0030	total	total
Silicon in hydrochloric acid residue.....	0.0097	0.0067	0.0049	0.0194	0.0144	0.0039
Phosphorus evolved by hydrochloric acid.....	0.0014	0.0017	0.0018	0.0020	total	total
Phosphorus in hydrochloric acid residue.....	0.0006	0.0006	0.0006	0.0004	0.0012	trace
Manganese.....	0.0003	0.0019	0.0034	0.0071	trace	none
Sulphur.....	.....	.....	.....	0.0003	.....	.....
Chromium.....	.....	.....	.....	.....	0.8995	.....
Tungsten.....	0.1471	0.1040	0.3056	.....	.....	0.9593
Molybdenum.....	0.0949	0.1346	0.0379	.....	.....	.....
Iron.....	0.7012	0.6086	0.6186	0.9347 D	0.0079	0.0007
Specific gravity.....	11.154	11.384	12.365	7.474	5.103	15.175
Formula.....	$\text{Fe}_{40}\text{Mo}_4\text{W}_4$	$\text{Fe}_{31}\text{Mo}_4\text{W}_9$	$\text{Fe}_{19}\text{Mo}_4\text{W}_{17}$	.....	.....	.....
Condensation from composition difference.....	2.898+	2.942+	3.438+	.....	.....	.....

D=by difference.

are characteristic of ferrochromium, attaining a very marked development which places them entirely outside the category of micro or sub-micro structure. I am in doubt as to whether the formula  $\text{Fe,Cr}_3\text{C}_2$  is meant to represent the needles, for this compound is described as "a coarse brownish grey lustrous powder, made of small bars, of which many are three to four mm. in length." The data are confessedly very scanty but against the iron derivation of the needles is to be placed the three compounds found in the ternary alloys whose constancy can hardly be ascribed to the constituent tungsten or molybdenum, metals chemically to be classed with chromium; and the existence of Moissan's carbide  $\text{Cr}_3\text{C}_2$ , an analogous compound. This is more clearly understood from Professor Garrison's description given later. That, however, the constitution of such compounds would be dependent on the composition of the mixture and would only be fairly constant within certain limits can be readily understood, as, for example, with double salts crystallizing in varying proportions; and hence when the iron becomes an unimportant factor in the composition of the alloy its influence would correspondingly wane in the compound crystallizing from the mixture, and vice versa. It is to be noted, moreover, that very little is known of the valence or combining power of the elements in metallic alloys and not only is this lacking for iron and chromium, but if the composition of the crystals is dependent on the composition of the alloy and the temperature at which they separate there may also be an alteration in the ratio in which iron and chromium combine, for valency may well be dependent on the temperature. Note that alloy II contains 12.07 per cent. of chromium but has a much greater content of chromium in the separated crystals than the compound of formula  $\text{Fe,Cr}_3\text{C}_2$ .

The separation of the crystals from the granular material was readily effected by the comparatively slight action of nitric acid which left the crystals as residue intermixed with a little silica. This was volatilized as silico-fluoride and after washing with water and subsequently with ninety-five per cent. alcohol the crystals were obtained free from impurity. Their reactions show them to be chemically very inert compounds. As stated, they are but little attacked by nitric acid, strong or dilute.

Hydrochloric or hydrofluoric acid does not attack them. Strong sulphuric acid slowly decomposes them leaving a black residue which still retains the form of the crystals. The solvent is useless as a means of analysis. By themselves the crystals are attacked but slowly by strong aqueous solution of bromine or of iodine and only on heating. However, in the residue obtained by treating the alloy with these reagents no trace of the crystals could be observed, using a lens magnifying fifty diameters. With reflected light the residues showed granular masses of irregular shape with brilliant metallic luster. From the mode of occurrence of the crystals in the alloy they could hardly have been absent from the samples examined. At a red heat chlorine, bromine, and iodine readily decompose them, but their analysis is best effected by fusion with an oxidizing mixture of sodium carbonate and saltpeter with addition of caustic soda.

Professor Garrison, in his discussion,<sup>1</sup> gives the form and dimensions of the crystals as follows: "I have examined under the microscope the segregations obtained from alloys II and V and find them to consist of well developed prismatic hexagonal crystals, more or less corroded by the nitric acid solvent. I was not able to detect any of the crystals with pyramidal terminations; most of them appeared to have been broken, leaving ragged ends, as would be observed in Figs. 1 and 2. The general appearance of the crystals from the different alloys is similar. Those from II averaged 0.03 to 0.04 of an inch in length, and 0.003 of an inch in diameter; those from V were 0.03 to 0.04 in length and 0.005 of an inch in diameter. The aspect of the crystals under a magnification of thirty-five diameters is well shown by the micro-photographs; Fig. 1 being from alloy II, and Fig. 2 from V, I was able to detect a slight difference in color between the two varieties when they were heaped in masses and held in the proper light. II had a decided yellowish metallic luster; V a dark steel-grayish-blue color and luster. The slight difference in thickness was not appreciable to the naked eye, neither would the color or luster be apparent to a casual observer. I experienced some difficulty in making the specific gravity determinations of these crystals, owing to

<sup>1</sup> Iron and Steel Institute, May meeting, 1895.

the extremely small quantities. On the whole, I think those mentioned are nearly correct, although that of II might be a light one." Of II specific gravity is 12.80; of V 7.473 (Garrison).<sup>1</sup>

The analytical results obtained were :

*Alloy V.—Ferromolybdenumchromium Carbide.* The analysis was made as follows : Half a gram of pure crystals were fused with the oxidizing mixture with addition of caustic soda. The melt was cooled, lixiviated in water, and the solution containing chromate and molybdate filtered from the residual ferric hydroxide. The solution was acidified with hydrochloric acid and boiled to dryness with addition of alcohol to ensure reduction of the chromic salt. The residue was then dissolved in a little dilute hydrochloric acid, diluted and brought to boiling. Chromium was precipitated by ammonia in excess, the boiling being continued for at least half an hour. The precipitated chromic hydroxide was filtered off, washed twice with hot water, dissolved in dilute hydrochloric acid, and reprecipitated by ammonia. This solution was filtered, the filtrate being added to the first but not the washings. The chromic hydroxide was now thoroughly washed by boiling up with water, decanting, finally throwing on the filter, and washing with boiling water. It was then dried, ignited, and weighed as  $\text{Cr}_2\text{O}_3$ . In analysis 1 (table II) the filtrate containing the molybdenum was boiled until the odor of ammonia had to a great extent disappeared. The solution was then acidified with sulphuric acid, poured into a separatory funnel containing zinc and, after reduction, titrated with permanganate (Pisani's method). In analysis 2 the molybdenum was determined gravimetrically. The ferric hydroxide was examined for silica but the quantity found checked closely with that present in the alkali salt used for fusion. After removal of platinum, iron was converted to sulphate and titrated in acid solution by permanganate. The chromic oxide was fused with bisulphate and the solution examined for phosphorus with nega-

<sup>1</sup> In some experiments carried out by Professor Garrison and myself with highly phosphoric titaniferous pig iron, prismatic needles were obtained lining the cavities and blow-holes. Their form could not be made out with certainty but they were well developed and in no sense belonged to the micro structure of the alloy. They have not yet been isolated. The prismatic form is of frequent occurrence in Ferromanganese.

tive results. If silicon or phosphorus were important constituents of the crystals they would readily be detected in a half gram sample. The carbon of analysis 1 was determined by direct combustion of the crystals with the lead and potassium chromate mixture. The carbon of 2 was determined by combustion of the residue obtained after first decomposing in chlorine at a red heat.

TABLE III. FERROMOLYBDENUMCHROMIUM CARBIDE.

	Analysis 1. Atomic ratio.		Analysis 2. Atomic ratio.	
Iron .....	0.4639	0.828	0.4650	0.830
Chromium .....	0.4623	0.882	0.4606	0.879
Molybdenum .....	0.0201	0.021	0.0194	0.020
Carbon .....	0.0553	0.461	0.0559	0.464

No manganese, silicon, or phosphorus were present. These results give the ratio  $\text{Fe}:\text{CrMo}:\text{C}::1.79:1.95:1$ , or formulated  $\text{Fe}_2(\text{CrMo})_2\text{C}_3$ . To this compound I give the name Wahlite, from Dr. William H. Wahl, well known for his valuable contributions to metallurgy.

Alloys II and II B. — *Ferrotungstenchromium Carbide*. In addition to the alloy (II) described in the first paper, a second alloy (II B) was made using 200 grams of iron in the melt instead of fifty. The object in doing so was to determine whether change in composition of the melt had any effect on the composition of the resultant crystals. The quantity of crystals obtained for analysis II was small. Iron, chromium, and tungsten were determined after purifying by nitric acid one gram of the original material. The residue was then analyzed and the calculations made to 100 per cent. For analysis II B abundant material was available. Considering the small quantities available for the first analysis the agreement is satisfactory. Comparing with alloy V it would appear that the ratio of chromium to iron is not the same in the two alloys. Tungsten and molybdenum probably play the same role as chromium and replace it perhaps in varying quantities. The analysis was made by decomposing the crystals as with alloy V. The solution containing tungstate and chromate was acidified with hydrochloric acid, alcohol added, and evaporated to dryness. The residue was taken up in dilute hydrochloric acid and an equal bulk of alcohol added.

The tungstic acid was filtered off, dissolved from silica by ammonia, the solution evaporated, and tungsten determined as  $\text{WO}_3$ . The filtrate containing chromium was brought to boiling and chromium hydroxide thrown down by ammonia. Alloy II, as obtained in original sample, contained iron 0.0423, chromium 0.0317, tungsten 0.0102. The analytical results gave :

TABLE IV. FERROTUNGSTENCHROMIUM CARBIDE.

	Alloy II.	Atomic ratio.	Alloy II B.	Atomic ratio.
Iron.....	0.4724	0.843	0.4723	0.843
Chromium .....	0.3542	0.676	0.3682	0.702
Tungsten .....	0.1139	0.060	0.1007	0.054
Carbon.....	0.0595	0.496	0.0599	0.494

No manganese, silicon, or phosphorus was present in II B. These results give the ratios :

Alloy II. Fe : CrW : C :: 1.69 : 1.49 : 1, or formulated  $\text{Fe}_2(\text{CrW})_2\text{C}_3$ .

Alloy II B. Fe : CrW : C :: 1.73 : 1.53 : 1, or formulated  $\text{Fe}_2(\text{CrW})_2\text{C}_3$ .

Carbon in both cases was determined by direct combustion of the crystals. To the compound I give the name Garrisonite, from Professor F. Lynwood Garrison, a valued contributor to the study of the microstructure of iron and to its metallurgy. Alloy II B contained, chromium 0.1070, tungsten 0.0871.

## ON THE POSSIBILITY OF THE OCCURRENCE OF HYDROGEN AND METHANE IN THE ATMOSPHERE.<sup>1</sup>

Received September 9, 1895.

BY FRANCIS C. PHILLIPS.

WHATEVER may have been the process by which organic remains have in the course of time been caused to yield gas and petroleum, a considerable portion of the gas evolved in the early stages of decay must have escaped into the atmosphere before the burial of such remains under sedimentary deposits, and the consequent imprisonment of the more volatile products could have occurred. This would have been the case if, as in the view of the older geologists, the source of gas and oil is to be looked for in the slow decomposition, at low temperatures, of

<sup>1</sup> Read at the Springfield meeting.

masses of seaweeds as they were gradually buried under accumulating sediments. It would have occurred likewise if, according to Engler's hypothesis, gas and oil have come from the distillation of animal remains under pressure of overlying sediments and at a gentle heat.

For a long interval of time must have elapsed between the commencement of decay and the final burial of such remains under marine deposits, of sufficient thickness and compactness, as to cause the retention of the hydrocarbons until the sediments became consolidated into rock.

In a paper upon the origin of natural gas<sup>1</sup> I have called attention to the great difference in the nature of the changes which may occur in organic remains submerged under water and protected from atmospheric influences. The early stages of the decay are rapid, and much hydrogen may be produced. The later stages are more gradual, and methane may be a chief product of the decay. At the beginning of the process the cell contents are chiefly concerned in the change. Even if buried under deep sediments the tumultuous nature of the gas evolution must cause the gas bubbles to break through and escape from dense masses of clay and sand.

The following experiment was described in the paper cited: A quantity of a seaweed was allowed to decay under water in an apparatus so constructed that any gas produced could be collected over mercury. Rapid decomposition soon set in and continued for ten days, when the evolution of gas apparently ceased, having become much retarded towards the end. In all 803 cc. of gas were collected. Analyses were made of the first portion of 300 cc., of a second portion of 300 cc., and of a third portion of 203 cc. The results are tabulated below:

	First portion.	Second portion.	Third portion.
Carbon dioxide.....	18.23 per cent.	32.47 per cent.	53.44 per cent.
Carbon monoxide..	0    "	0    "	0    "
Ethylene .....	0    "	0    "	0    "
Methane.....	0.30   "	0.28   "	0.08   "
Hydrogen.....	62.24   "	48.97   "	42.02   "
Nitrogen.....	19.23   "	18.28   "	4.46   "
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00



The temperature during the experiment did not exceed 20° C.

The same apparatus was kept in position for two and one-half years after the above experiment was made. During this time a continuous production of gas was observed, but it was so slow that at the end of this period only about 30 cc. of gas had collected. This was found to consist of methane.

Frankland & Jordan<sup>1</sup> found that grease left to decay under water, air being excluded, evolved gas of the following composition :

	In 3 days.	In 3 days.	In 4 days.
Carbon dioxide.....	84.63	87.66	84.41
Oxygen.....	0.13	....	....
Hydrogen.....	6.90	8.75	9.17
Other combustible gases .....	2.51	0.71	0.27
Nitrogen.....	5.83	2.88	2.15

I have examined gas collected from swamps in many localities. Gas samples have been taken from streams having muddy bottoms and in which vegetable remains had accumulated. Carbon dioxide, nitrogen and methane are usually found in shallow swamps. In deeper swamp waters, where masses of vegetable debris of greater thickness occur, hydrogen is often found in small quantities mixed with carbon dioxide, nitrogen and methane.

According to the hypothesis of Mendeleeff natural gas and petroleum have been produced by the action of steam at high temperatures upon the metallic compounds of carbon.<sup>2</sup> The general result of experiments upon the action of steam upon the heated carbides of iron, manganese and other metals, has been to show that in all such cases there is produced mainly hydrogen mixed with relatively small quantities of hydrocarbons. It is found, however, that the natural gas which flows from the wells of Pennsylvania, New York, West Virginia, Ohio, and Indiana, consists mainly of methane with small quantities of other hydrocarbons, but does not contain free hydrogen. Hence if we accept the hypothesis of Mendeleeff we must suppose that the natural gas, now flowing from the earth in such vast quantities, represents the diminished residue of a much larger volume

<sup>1</sup> J. Chem. Soc. (Lond.) 1883, p. 295.

<sup>2</sup> Mendeleeff : Principles of Chemistry, I, 365.

of gas from which the free hydrogen has escaped through the overlying rocks. Whatever view is adopted as to the origin of natural gas there seems to be good reason to believe that considerable volumes of hydrogen and of gaseous paraffins have found their way into the atmosphere, and that the process has been continuous since early geological times.

Evolution of carbon dioxide from organic remains is merely one stage in a cycle of changes. The carbon dioxide present in the atmosphere parts with its carbon to growing plants. They, in their turn, yield back carbon dioxide as they die and decay. On the other hand each bubble of hydrogen and of methane, once set free at the earth's surface, probably escapes unoxidized and unabsorbed to ascend into the higher strata of the atmosphere.

Of all the forms which hydrogen and carbon can assume in nature, free hydrogen and methane are among the most stable and unalterable as regards all influences at the earth's surface. Their slight solubility in water protects them still further from oxidation.

In the natural gas regions gas bubbles are easily produced by stirring up the sediments at the bottom in streams, ponds and rivers. This is not only the case where decaying vegetation occurs, but in streams flowing over gravel and pebbles where no decay is in progress. The loose gravel appears merely to arrest temporarily the gas on its way out from the earth and renders it visible as it escapes in bubbles through the water. If the gas accumulated under gravel and sand in streams be dislodged by stirring it is usual to find that, in a day or two, or even after a few hours, it has again collected in considerable quantity. Constant agitation of the gravel seems not to diminish the amount of the gas flow.

Such emanations of gas are common in Western Pennsylvania and Western New York, in regions where the occurrence of hard rock directly below the gravel bed of a stream precludes the supposition that the gas has resulted from the decay of recently buried tissues. It is probable that the gas which is continually accumulating in such situations is derived from great depths, that its presence is the result of a slow process of diffusion from

below, which only terminates as the gas enters the atmosphere, and that it constitutes a considerable portion of the natural gas which was stored originally in the rocks.

The feebly luminous flame produced by this gas distinguishes it from the nitrogen, which so frequently collects in the sands of river beaches in regions of constant fluctuations of water level due to tides, and where organic remains are abundant.

In the latter case the air penetrating the sand at low tide parts with its oxygen to the decaying matter, and as the tide rises again the residual nitrogen is expelled in bubbles under the pressure of the advancing water, while the carbon dioxide formed is retained in solution.

Gas collected from the gravel bottom of a stream flowing into the Ohio river near Sewickley, Pa., was found to have the following composition :

	Per cent.
Methane .....	93.06
Nitrogen .....	6.70
Carbon dioxide .....	0.24
	<hr/> 100.00

There is no reason to suppose that the diffusion of gas from the earth into the atmosphere is confined to surfaces covered by water, although it can only be made visible by the formation of bubbles in water.

It is no doubt continually in progress in regions of Devonian and carboniferous rocks.

This slow diffusion of gas from the earth into the atmosphere has occurred since early geological times and in regions where erosion has finally carried away whole systems of sedimentary rocks, liberating the imprisoned hydrocarbons by slow degrees. The gas thus escaping from within the earth's crust is added to that which is derived from recent decay on the surface, and probably forms no inconsiderable part of the total quantity carried continually into the atmosphere.

Hydrogen in a limited volume of air follows the well-known law of diffusion, mixing completely with the air.

Should a large mass of hydrogen enter the earth's atmosphere, the case would be different. Hydrogen, while it would diffuse

laterally with the air, would tend to accumulate in the upper strata on account of the great difference between its specific gravity and that of the constituents of the air. Ferrel,<sup>1</sup> has fully discussed the hypothetical case of the occurrence and arrangement of a very light constituent in the atmosphere, "Where the relative densities of the constituents regarded as independent atmospheres, would be nearly the same at the different altitudes, as in the case of oxygen and nitrogen, a constant agitation of the whole may keep them so mixed up that the proportions are nearly the same at all altitudes; but, in the case of a very rare constituent, the tendency would be for it to rise up so far above all the others that it could not become mixed up with them except in the lower strata, and at a considerable altitude it would be the only sensible constituent unaffected by the agitation of the comparatively much denser constituents which would exist, only sensibly lower down, near the earth's surface."

If the presence of hydrogen is ever positively detected in the atmosphere, it must be looked for in air samples collected as far away from the earth's surface as possible.

An experimental demonstration of the presence or absence of hydrogen in air, would be of great interest if the method to be employed were certain as regards its results. Existing methods for the detection or determination of hydrogen when present in traces, are not satisfactory.

After many trials, I have devised a method for the detection of traces of free hydrogen in a gas mixture. The method consists, briefly, in passing the gas over anhydrous palladium chloride contained in a glass tube. Free hydrogen reduces this salt at once, and in the cold, being converted into hydrochloric acid, which is recognized by passage through a silver nitrate solution.

Having in palladium chloride a reagent of extreme delicacy for free hydrogen, it seemed to be of interest to attempt a test for hydrogen in air, and in order to avoid as far as possible, all danger of impurities from local conditions at the earth's surface, some experiments were tried on Mount Washington, New Hampshire, during August, 1892.

<sup>1</sup> Annual Report of the Chief Signal Officer of the Army for 1885, pt. 2, p. 41.

The elevation of Mount Washington, nearly 7000 feet, did not justify the belief that upon its summit strata of air materially different from those at sea level could be reached, but there was the undoubted advantage of greater purity and freedom from local contamination.

By permission of Mr. Mark Harrington of the U. S. Agricultural Department, a room in the Weather Observer's building on the mountain, was used for the purpose.

I desire here to express my appreciation of the courtesy shown by Mr. Harrington and also by Mr. Mitchell in charge of the station, in affording facilities for the work.

Details of the work are omitted, as the results of two very carefully conducted experiments were negative, and therefore did not lead to a definite conclusion.

It may be suggested that ozone, by reason of its great oxidizing power, would tend to prevent the accumulation of combustible gases in the upper atmosphere. Oxygen is well known to derive its active properties from the influence of the electric discharge.

Ozone may be produced locally in considerable quantity as a result of violent electrical disturbances in the atmosphere. Much of the ozone thus formed probably expends its power in oxidizing atmospheric nitrogen to nitrous and nitric acid.

Ozone has a specific gravity much greater than oxygen, and would, consequently, tend to descend rather than to rise to the outer limits of the atmosphere. While the production of ozone must occur at points remotely distant and at considerable intervals of time, the evolution of hydrogen and methane at the earth's surface is continuous. Moreover, thunderstorms only occur during a brief portion of the year in temperate climates, and are unusual at all times in far northern latitudes.

In view of these facts it seems improbable that ozone can be considered likely to materially retard an accumulation of the lighter gases, hydrogen and methane, in the upper atmosphere.

Hydrogen and methane are not oxidized by prolonged contact with a two per cent. solution of hydrogen peroxide at 20° C.

It is true that the upper air may contain nitrous acid. Paper coated with potassium iodide and starch was found to be rapidly turned purple when exposed on Mount Washington. Free

hydrogen is, however, not oxidized by fuming nitric acid<sup>1</sup> and it is hardly likely that nitrous acid, in the highly diluted condition in which it must be looked for in air, could cause an oxidation of hydrogen.

Meyer<sup>2</sup> and Askenasy found that on exposure to bright sunlight, a mixture of oxygen and hydrogen suffered no change. Combination did not occur even on exposure of the gas to a temperature of 600° C.

Meyer and Seubert<sup>3</sup> have shown that under highly reduced pressure combination does not occur in a mixture of oxygen and hydrogen under the influence of the electric spark. Experiments with mixtures of various hydrocarbons with oxygen, led to similar results. The minimum pressures at which the electric spark caused an explosion, were about one-tenth of an atmosphere in the case of hydrogen, and one-sixth of an atmosphere in the case of methane. In earlier times Humphrey Davy was led to similar conclusions as regards the explosion of rarified gas mixtures.

Although the minimum pressure at which chemical union would occur, may vary with the character of the discharge, it may be asserted that electrical disturbances are less likely to influence the oxidation of these combustible gases in the higher atmosphere where they must be looked for, if present in the atmosphere at all.

Methane and hydrogen possess under all conditions, great resistance toward oxidizing agents, and, once set free in air, it is questionable whether either gas could undergo any change by which it might be wholly brought back within the sphere of reactions produced by organic life, or by oxygen. Ferrel has suggested that the hydrogen of the sun's atmosphere may form merely an outer layer, resting upon much denser gases below.<sup>4</sup> It is possible, at least, that such an arrangement exists in the earth's atmosphere.

It seems desirable that tests for hydrogen and methane in air, should be made at still greater altitudes in order that more defi-

<sup>1</sup> Winkler: *Ztschr. anal. Chem.*, 1889, 269.

<sup>2</sup> *Ann. Chem.* (Liebig), 269, 72.

<sup>3</sup> *J. Chem. Soc.* 1884, 587.

<sup>4</sup> *Loc. cit.*

nite information may be gained upon this interesting subject, although serious difficulties would be encountered in attempting to reach an altitude so high as to render the results of chemical tests positively conclusive.

WESTERN UNIVERSITY LABORATORY,  
ALLEGANY, PA.

### A NEW GENERATOR.

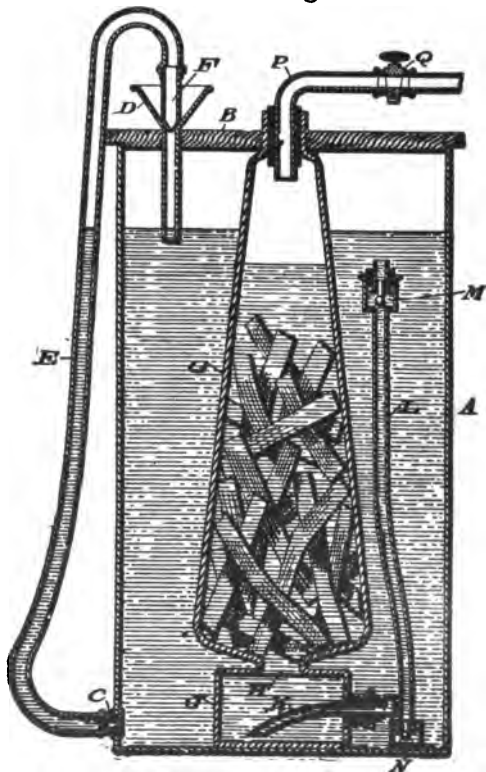
BY EDWARD P. HARRIS.

Received May 27, 1895.

A GREAT many forms of automatic generators for the preparation of such gases as hydrogen, hydrogen sulphide, carbon dioxide, etc., have been proposed, that known as the "Kipp apparatus" being probably most widely used.

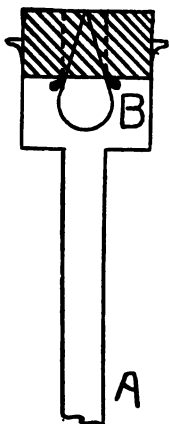
The chief objection to this and other forms in general use lies in the fact that according to their construction the spent acid at the bottom of the reservoir, containing the metallic salts, is used over and over again until it becomes too weak for further action, while plenty of fresh acid remains in the upper part of the reservoir, unable to enter the inner chamber containing the solid material (zinc, iron sulphide, marble, etc.)

The accompanying figures show how this difficulty is removed by a very simple device. The second figure shows the side

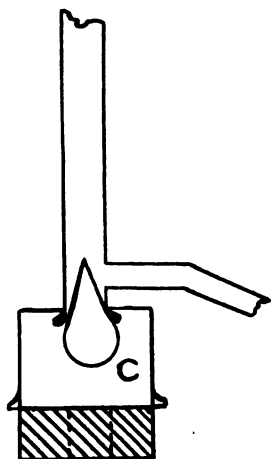


tube A enlarged. By mistake the artist has placed the side tube on the wrong side.

The bottom of the inner cylinder is closed and the flow of acid must be through the side tube A. This tube is connected with the lower part of the inner cylinder and is entirely immersed in the acid of the reservoir. At each end is a floating glass valve playing upon a rubber cushion at the end of the tube. When the gas is turned on and the pressure relieved from the inner cylinder the acid can enter only at B, and when the action is reversed the acid can escape only at C.



Thus, fresh acid from the upper part of the reservoir is always used and the spent acid containing the metallic salts is always deposited at the bottom where it remains, owing to its greater specific gravity. Once set up and charged the only attention this generator needs is the occasional withdrawal of some of the spent acid from the bottom and the addition of an equal quantity of fresh acid through the funnel at the top.



A generator of this description two and a half feet in height has furnished hydrogen sulphide for a class of thirty students in qualitative analysis for eight months, the only attention required being to fill the reservoir three times with acid. The apparatus may be obtained from Queen & Co. in three sizes. The largest size is particularly recommended for generating hydrogen sulphide.

CHEMICAL DEPARTMENT OF THE PENNSYLVANIA MILITARY COLLEGE,  
CHESTER, PA.



## THE DETERMINATION OF TANNIN BY METALLIC OXIDES.<sup>1</sup>

BY WILLIAM H. KRUG.

Received September 6, 1895.

THE following experiments were suggested by a method proposed for the estimation of tannin by Mr. Kerr, associate reporter on tannin, during the progress of the official work for the Association of Official Agricultural Chemists. This method consisted of the percolation of the tannin-bearing liquor through a column of asbestos with which a certain amount of yellow mercuric oxide had been intimately mixed. After making a number of attempts to obtain concordant results, I found it too difficult to secure uniform conditions such as rate of percolation, extent of contact and uniformity in the asbestos layer, and therefore turned to find some other way of using the oxide. It then occurred to me to substitute it for the hide-powder in the ordinary shaker method. During the work I extended the investigation to three other oxides, *viz.*, magnesium, zinc, and lead oxides.

At the beginning it was evident that much more time would be consumed in absorbing the tannin in this manner and a number of preliminary experiments were made to determine this time limit if possible. In all cases when, upon filtration after shaking a certain length of time, it was found that combination was incomplete, the solution was allowed to stand until this was accomplished. It was thus found, that with magnesium and mercuric oxides, it was best to shake about four hours and then let the mixture stand over night, when it would be ready for filtration.

With lead oxide the process required two days, after being shaken four hours, and the mixtures with zinc oxide stood a week before the tannin was totally absorbed. These two oxides were, therefore, rejected as requiring too much time, though the analyses made with them, are given below for comparison.

The extract used contained 42.35 per cent. soluble solids, and the diluted liquor used in the analyses, contained two grams of this extract per 100 cc. This diluted extract gave in twenty-

<sup>1</sup> Read at the Annual Meeting of the Association of Official Agricultural Chemists, Sept. 5, 1895.

five cc. as a mean of three determinations, 0.0113 gram ash, containing 0.0006 gram magnesium oxide.

The tannin was determined by the loss in solids, *i. e.*, twenty-five cc. of the filtrate were evaporated on the steam-bath in a weighed dish, dried three hours in a water-bath, and the weight of the residue determined. The difference between this weight and the solids in twenty-five cc. of the original diluted extract, was taken as tannins. The ash determinations were made as a check on the amount of the oxide dissolved during the analysis.

#### Experiments with zinc oxide.

Method.	Grams ZnO used.	cc. di- luted extract used.	cc. of filtrate evaporated.	Weight of residue.	Per cent. tannin in extract.	Grams ash in residue.	Grams ZnO in ash.
Shaken 4 hours, stood over night....	2.0	75	25	0.1095	20.45	0.0125	0.0008
" 4 " " " " ....	2.0	75	25	0.1174	18.87	0.0147	0.0019
Shaken 4 hours, stood one week....	2.0	75	25	0.1049	21.37	0.0095	....
" 4 " " " " ....	2.0	75	25	0.1029	21.97	0.0103	0.0030
" 4 " " " " ....	2.0	75	25	0.1029	21.97	0.0100	0.0020

The first two of these analyses gave a faint reaction for tannin, but were run through so as to compare the result with those obtained with other oxides. The low figures indicate incomplete combination. The last three gave no test for tannin when filtered, and agree fairly well. They are low, compared with lead and mercury oxides, and agree better with the results obtained with magnesium oxide. The amount of zinc oxide dissolved is too small to affect the accuracy of the analysis, and the only objection to the use of this oxide is the slow action. The last three analyses were tested every day for a week, before it was found that all the tannin had been absorbed. For this reason zinc oxide would be of no value in a laboratory where the rapid estimation of tannin is desired.

#### Experiments with lead oxide.

Method.	Grams PbO used.	cc. di- luted extract used.	cc. of filtrate evaporated.	Weight of residue.	Per cent. tannin in extract.	Weight of ash from residue.	Grams PbO in ash.
Shaken 3½ hours, stood 2 days....	4.0	75	25	0.0738	27.59	0.0111	0
" 3½ " " 2 " ....	4.0	75	25	0.0754	27.27	0.0092	0
" 3½ " " 2 " ....	4.0	75	25	0.0706	28.23	0.0105	0

None of these gave a reaction for tannin with ferric chloride. The results were higher than with any other oxide used. The objection to lead oxide is the length of time required for complete combination.

## Experiments with magnesium oxide.

Method.	Grams MgO used.	cc. di- luted extract used.	cc. filtrate evapo- rated.	Weight of residue.	Per cent. tannin in extract.	Weight ash in resi- due.	Weight MgO in ash.
Shaken 2½ hours, stood over night...	2.0	75	25	0.1134	19.67	0.0209	0.0055
" 2½ " " " "	2.0	75	25	0.1028	21.79	0.0195	0.0042
" 2½ " " " "	2.0	75	25	0.1230	17.75	0.0232	0.0052
" 2½ " " " "	2.0	75	25	0.1246	17.43	0.0247	0.0058
Stood 24 hours with occasional sh'k'g	2.0	75	50	0.2063	21.72	0.0252	0.0074
" 24 " " " "	2.0	75	50	0.2061	21.74	0.0244	0.0076
" 24 " " " "	2.0	75	25	0.1157	19.21	0.0213	0.0044
" 24 " " " "	2.0	75	25	0.1114	20.07	0.0205	0.0038
" 48 " " " "	2.0	75	50	0.1941	22.94	0.0326	0.0064
" 48 " " " "	2.0	75	50	0.1959	22.76	0.0339	0.0070
Shaken 3½ hours, stood over night...	2.0	75	50	0.2165	20.70	0.0349	0.0102
" 3½ " " " "	2.0	75	50	0.2191	20.44	0.0355	0.0111
" 3½ " " " "	2.0	75	50	0.2179	20.56	0.0359	0.0115

This table shows that a considerable amount of the oxide is dissolved, and passes into the filtrate, increasing the weight of the residue, and correspondingly lowering the tannin. That this error may be quite considerable is shown by the fact that in almost every estimation, the ash is almost double that found in the original diluted extract. Furthermore, this error does not seem to be constant, so that no correction can be made for it.

## Experiments with mercuric oxide (yellow).

Method.	Grams HgO used.	cc. di- luted extract used.	cc. filtrate evapo- rated.	Weight of residue.	Per cent. tannin in extract.	Weight ash in resi- due.	Weight HgO in ash.
Stood 48 hours with occasional sh'k'g	4.0	75	25	0.0833	25.69	0.0070	0
" 48 " " " "	4.0	75	25	0.0829	25.77	0.0077	0
" 48 " " " "	4.0	75	25	0.0829	25.77	0.0071	0
Shaken 1½ hours, stood over night...	4.0	75	25	0.0842	25.51	.....	..
" 2 " " " "	4.0	75	25	0.0867	25.01	.....	..
" 3½ " " " "	4.0	75	25	0.0863	25.09	0.0081	0
" 3½ " " " "	4.0	75	25	0.0860	25.15	0.0080	0
" 4 " " " "	4.0	75	25	0.0839	25.57	0.0084	0
" 4 " " " "	4.0	75	25	0.0849	25.37	0.0065	0
" 4 " " " "	4.0	75	20	0.0638	26.41	0.0065	0
" 4 " " " "	4.0	75	20	0.0692	25.05	0.0103	0
" 4 " " " "	4.0	75	20	0.0682	25.29	0.0094	0
" 4 " " " "	4.0	75	25	0.0863	25.09	0.0083	0
" 4 " " " "	4.0	75	25	0.0849	25.37	0.0097	0
" 4 " " " "	4.0	75	25	0.0842	25.51	0.0084	0

The above analyses show that even though the conditions may be varied, fairly concordant results can be obtained with mercuric oxide as long as care is taken to ensure the complete absorption of the tannin before filtering. The end of the reaction may be easily observed, since, when it is reached, the yellow oxide

no longer sinks to the bottom, but the whole mass partially gelatinizes and becomes dirty brown. A clear filtrate free from tannin and mercury can then be readily obtained.

The results in the ash column show that a certain amount of the ash present in the extract is held back, but this error is quite constant and so small as to have little influence on the result. Although the time required for the analysis of a tannin-extract by this method is somewhat longer than with hide-powder, still the uniform results obtained more than compensate for this, and, at the most, an analysis will not take more than two days. A number of analyses can be made at a time by adapting a shaker so as to hold several 100 cc. sugar flasks, which are of a convenient size for this work.

---

### THE ESTIMATION OF SULPHUR IN REFINED COPPER.<sup>1</sup>

BY G. L. HEATH.

Received September 9, 1905.

SEVERAL general methods for the estimation of sulphur in copper have been published, most of which are defective, or not accurate for all classes of work.

It is the writer's purpose to call attention to these processes, and then to present the results of some experiments, and an improved method, devised especially for the determination of traces of sulphur.

R. Fresenius<sup>1</sup> proposed to treat twenty grams of copper with strong nitric acid, nearly neutralize with ammonia, add a few drops of barium nitrate and allow to stand for several hours. As stated by the same authority, very small quantities can not be separated in this way, since barium sulphate is somewhat soluble in copper nitrate.

For small amounts of sulphur, W. Hampe's "chlorine" process has been recommended. This consists in heating thirty grams of the metal in a glass tube in a current of pure, dried chlorine gas. The sulphuric acid evolved, is absorbed by water saturated with chlorine.

From personal experience, the method is not judged to be a

<sup>1</sup> Read at the Springfield Meeting.

<sup>2</sup> *Ztschr. anal. Chem.*, 13, 223.

very accurate one, for there are two or three possible sources of error.

1. The existence of the sulphur in different forms.
2. The incomplete removal of all oxygen and other impurities, from the chlorine gas.
3. The occasional formation of a layer of melted chloride, which may prevent the complete evolution of sulphur and combustion of copper.

A third method involves the use of potassium permanganate.

A fourth, and apparently, the most direct and satisfactory one, consists in dissolving ten grams of copper in nitric acid, or in a mixture of nitric with a little hydrochloric acid, and then precipitating the sulphuric acid directly from a hydrochloric acid solution, after removing all the nitric acid by repeated evaporation.

Upon this principle depends the method of H. J. Phillips.<sup>1</sup>

But the writer has repeatedly attempted to test refined copper by the last method, without obtaining any precipitate of barium salt. There should have been at least a trace of precipitate due to sulphur in the chemical reagents.

Though no refining on the large scale has ever produced metal in which a chemist could not find a trace of impurity, yet the best American refined copper of to-day, contains such a minute amount of sulphur, that a very delicate and accurate method is required for its estimation.

In order to test the influence of copper chloride and free hydrochloric acid upon barium sulphate, some experiments were made with solutions of pure copper chloride, and sulphuric acid.

It is a well known fact that certain substances interfere with the precipitation by barium chloride, and that barium sulphate is somewhat soluble in certain acids, and in solutions of copper.

The work of R. Fresenius,<sup>2</sup> F. W. Mar,<sup>4</sup> and others, has indicated that an excess of hydrochloric acid promotes the complete separation of barium sulphate, a conclusion rather contrary to earlier opinions.

<sup>1</sup> *Chem. News*, 62, and *J. Anal. Appl. Chem.*, 5, 53.

<sup>2</sup> *Ztschr. anal. Chem.*, 9, 52 and 62, also *Fres. Quant. Anal.*, Am. Ed. p. 139.

<sup>3</sup> *Am. J. Sci.*, 41, April 1891, also *J. Anal. Appl. Chem.*, 5, 278.

Mr. Mar states, as the writer has also noted, that the precipitation of minute quantities of barium sulphate is very much slower than that of large amounts.

Since the barium sulphate is not absolutely insoluble in water or dilute acid, the amount which would remain dissolved by a large volume of solution is appreciable, and cupric chloride may considerably influence the solubility.

As far as the time permitted, the experiments were carried out in two series; those analyses marked *a*, containing but a few drops of free hydrochloric acid, and those marked *b*, *c*, or *d*, about three and a half per cent. by volume of the same acid of 1.20 sp. gr.

Stock solutions were prepared as follows:

*a*. Standard sulphuric acid—1 cc.=0.00245 gram  $\text{BaSO}_4$ .

*b*. Cupric chloride solution—100 cc.=10 grams copper.

The solution used for all the experiments (except Nos. 12 *c*. and 12 *d*) was made by dissolving 100 grams of a very pure refined copper in 400 cc. of pure nitric acid, (sp. gr. 1.42), then precipitating the silver with a few drops of hydrochloric acid and filtering it off. The solution was then evaporated to dryness, and the evaporation repeated four times, with the addition of hydrochloric acid each time. The heat was continued until the chloride melted. The salt finally dissolved in water to a clear, faintly acid solution, which was diluted to one liter.

The slight trace of sulphur in the copper, was not any more than that found in the chemical reagents.

Ten grams of the copper yielded, by the author's method, only 0.0017 gram of barium sulphate, and the acids required for solution, gave 0.003 gram, for which allowance was made in the table of results.

*c*. As a check, some of the same copper was deposited by electrolysis from a nitric acid solution, and the pure plate was then redissolved, and after further treatment, the solution was used for experiments 12 *c*. and 12 *d*, in which one cc. standard sulphuric acid was added to the diluted copper solution.

The measured portions of copper salt, water and acid were placed in beakers and the standard sulphuric acid run in from a

burette. The liquids were heated to boiling, treated with two to five cc. of a saturated solution of barium chloride, stirred, and allowed to stand at the temperature of the room for the number of hours specified in the table.

The precipitates of the tests marked (*b, c, d,*) were washed first with five cc. of dilute hydrochloric acid, (one part acid to twenty of water) and then with hot water. The ones marked (*a*) were washed with hot water only, and in two or three cases, a trace of copper was not washed out. (See experiments 11*a*, and 15*a*).

At least a few drops of dilute acid should be always used in the first washing by decantation.

The results are tabulated according to the degree of dilution, and the weight of copper in the solution:

TABLE I.

ONE-TENTH GRAM OF COPPER IN SOLUTION. TOTAL VOLUME OF SOLUTIONS SEVENTY CC.

Faintly acid two-tenths free hydrochloric acid.					Strongly acid two and a half cc. hydrochloric acid added.				
Time in		Gram barium sulphate.		Difference.	Time in		Gram barium sulphate.		Difference.
No.	hours.	Taken.	Found.		No.	hours.	Taken.	Found.	
1 <i>a</i>	24	0.0025	0.0027	+0.0002	1 <i>b</i>	24	0.0025	0.0027	+0.0002
2 <i>a</i>	24	0.0123	0.0127	+0.0004	2 <i>b</i>	24	0.01235	0.0124	0.0000
3 <i>a</i>	24	0.04905	0.0489	—0.00015	3 <i>b</i>	24	0.0491	0.0497	+0.0006

TABLE II.

ONE GRAM OF COPPER IN SOLUTION. TOTAL VOLUME OF SOLUTIONS, 350 CC.

Slightly acid two-tenths cc hydrochloric acid.					Strongly acid 12.5 cc. hydrochloric acid.				
Time in		Gram barium sul-		Difference	Time in		Gram barium sul-		Difference.
No.	hours.	Taken.	Found.		No.	hours.	Taken.	Found.	
4a	24	0.0029	0.0026	—0.0003	4b	24	0.0029	0.0009	—0.0020
5a	24	0.0126	0.0115	—0.0011	5b	24	0.0126	0.0101	—0.0025
6a	24	0.0495	0.0446	—0.0049	6b	34	0.0495	0.0385	—0.0110
6a	72	0.0495	0.0490	—0.0005	6b	72	0.0495	0.0493	—0.0002
7a	72	0.2455	0.2445	—0.0010	7b	72	0.2462	0.2500	+0.0038

TABLE III.

TWO AND A HALF GRAMS OF COPPER IN SOLUTION. TOTAL VOLUME 350 CC.

Slightly acid two-tenths cc. hydrochloric acid.					Strongly acid 12.5 cc. hydrochloric acid added.				
No.	Time in hours.	Gram of barium sulphate.		Difference.	No.	Time in hours.	Gram of barium sulphate.		Difference.
		Taken.	Found.				Taken.	Found.	
8a	24	0.0036	0.0007	-0.0029.	8b	24	0.0046	0.0000	-0.0036
					8c	72	0.0936	0.0006	-0.0030
9a	72	0.0135	0.0129	-0.0006	9b	72	0.0036	0.0014	-0.0022
					9c	72	0.0135	0.0128	-0.0007
10a	72	0.0502	0.0496	-0.0006	9c	140	0.0145	0.0131	-0.0014
					10b	24	0.0502	0.0493	-0.0009
					10c	72	0.0502	0.0492	-0.0010
					10d	140	0.0502	0.0501	-0.0001
11a	72	0.2470	0.2505?	+0.0035	11b	72	0.2470	0.2486	+0.0016

TABLE IV.

TEN GRAMS OF COPPER IN SOLUTION. TOTAL VOLUME 700 CC.

Faintly acid one-half cc. hydrochloric acid.					Strongly acid twenty-five cc. hydrochloric acid added.				
No.	Time in hours.	Gram barium sulphate.		Difference.	No.	Time in hours.	Gram barium sulphate.		Difference.
		Taken.	Found.				Taken.	Found.	
		0.0074	0.0000	-0.0074					
12a	24	0.0074	0.0000	-0.0074	12b	24	0.0074	0.0000	-0.0074
					{ 12c	140	0.0057	0.0005	-0.0052 }
					{ 12d "		0.0057	0.0004	-0.0053 }
13a	72	0.0170	0.0102	-0.0018			0.0165	0.0014	-0.0151
					13b	24	0.0165	0.0013	-0.0153
14a		lost			13c	72	0.0165	0.0051	-0.0114
					14b	24	0.0540	0.0502	-0.0038
					14c		0.0540	0.0400	0.0140
15a	72	0.2509	0.2551?	+0.0047	15b	24	0.2500	0.2389	-0.0111
						72	0.2500	0.2436	-0.0064
						140	0.2500	0.2474	0.0026

The results, given in Table I., show that if the total volume of a solution is not over 100 cc. the barium sulphate is completely precipitated, whether the liquid is strongly acidified or not.

Table II: If the volume of the solution is increased to 350 cc. and the copper to two and a half grams, the precipitation is complete, even then, under the given conditions, in 72 hours with the exception of the analysis containing but a trace of sulphuric acid.



Tables III and IV : In the presence of as much as ten grams of copper in solution, the deposition becomes very slow indeed, as the results prove, and the strongly acidified solutions, at least retain appreciable amounts of barium sulphate.

Since the solubility of barium sulphate varies according to the conditions somewhat, the figures given by Fresenius, F. W. Mar, and others would not express the true effect of the water and dilute hydrochloric acid if the conditions of acidity, temperature, dilution, etc., were not the same. So a few experiments were made to determine the solvent effect of the water and acid alone.

Analyses 16-20 indicate that a part at least of the deficiency noted in the other tables is due to the solubility of the precipitate in the large volume (700 cc.) of dilute acid.

TABLE V.

No.	cc. of hydrochloric acid.	Temperature during settling.	Total volume.	Time in hours.	Gram barium sulphate.		
					Taken.	Found.	Difference.
16	25	20° C.	700	48	0.0025	0.0008	—0.0017
17	25	20° C.	700	48	0.0123	0.0086	—0.0037
18	25	20° C.	700	48	0.0490	0.0470	—0.0020
19	2 cc. + 5 grams ammonium chloride.		70	3	0.0490	0.0487	—0.0003

Fresenius<sup>1</sup> states that 1,000 parts of cold hydrochloric acid containing 3 per cent. dissolve 0.06 parts BaSO<sub>4</sub>.

Other experiments proved, however, that if a solution be kept at a temperature above 75° C., after the addition of barium chloride, the separation of barium sulphate is far more rapid and complete.

Cupric chloride appears to retard the deposition, especially when strongly acidified.

Direct precipitation in a moderately acid solution of this salt is determined to be sufficiently accurate for mattes and crude copper, but the separation of minute amounts of barium sulphate, from a very large volume of chloride solution, is too uncertain to permit the use of such a method for the detection and estimation of traces of sulphur in the best modern refined copper.

<sup>1</sup> F. Quant. Anal., 1st Am. Ed., p. 139, from Anal. Chem., 9, 62.

In 1889 the late Dr. L. M. Norton and the author of this paper devised and adopted a simple method, which has been improved by the latter, and has given very accurate results.

The complete precipitation of the barium sulphate is made possible in every case by first removing the copper electrolytically and then treating the solution as in the following scheme:

Take for analysis sufficient copper to yield a weighable amount of barium sulphate—ten grams will usually be enough.

Dissolve in a large beaker, placed over an alcohol flame, by means of a mixture of 60 cc. nitric acid (1.42 sp. gr.) and 15 cc. of hydrochloric acid (1.20 sp. gr.).

When dissolved, raise the lamp wick and evaporate nearly to dryness, then evaporate again after adding 50 cc. strong nitric acid.

Repeat this operation with another portion of the same acid, then redissolve in 300 cc. of water, and add a little nitric acid if a trace of basic salt remains undissolved.

The addition of hydrochloric acid and the consequent evaporation with nitric may be dispensed with, if experiment shows that nitric acid alone will oxidize all the sulphur in the class of material operated upon.

Next, pour the liquid through a small filter into a 700 cc. beaker and dilute with distilled water to 600 cc. or more.

Introduce as a negative electrode a large cone, or as is more convenient, a sheet of platinum, 4 by 5 inches.

Any wire or small piece of platinum foil will serve as a positive electrode.

Cover the beaker with glass and connect the electrode, preferably with an Edison incandescent lamp circuit.

The current from two sixteen candle-power lamps, coupled in parallel, will deposit the copper in one night.

When the liquid is colorless, or nearly so, remove the electrodes and wash them with distilled water, allowing the water to run into the main solution.

Pour off the liquid, if clear, from any bits of spongy copper, washing these on a small filter.

In order to prevent the escape of any sulphuric acid during subsequent evaporation, add, at this point, one-tenth gram dry,

pure sodium carbonate, (or a half gram for crude copper).

Evaporate the solution to dryness, as rapidly as possible without loss, in a No. 3 or No. 4, porcelain casserole. An alcohol lamp should be used, and the dish protected from dust. The evaporation may be completed on the water-bath, but if the dish is covered near the end of the operation and the flame regulated, there need be no loss by spattering, though the liquid be taken to dryness over the lamp. As soon as the salts in the dish are dry, heat the covered casserole quite strongly, with the lamp held in the hand, until the acid ammonium nitrate suddenly volatilizes, and then allow it to cool.

At this point is the only danger of loss of sulphur, and the heat should be just high enough to volatilize the nitrate. This heating may possibly be omitted if there is but a trace of ammonium nitrate in the dish. (See experiment 19).

Add to the residue, ten cc. strong hydrochloric acid and five cc. water, and evaporate to dryness on the water-bath. Repeat the process and then add one cc. of strong hydrochloric acid, add fifty cc. of water and dissolve, filter into a small beaker and wash the filter with hot water.

If the copper is known to be high in sulphur, the solution may be diluted to 150 cc. or more.

The only impurity of copper which might interfere with this method is lead. If lead is present, it will mostly remain in solution and be deposited on the plate, but if any lead sulphate remains on any of the filters, they must be boiled with a little solution of pure sodium carbonate, the solution filtered, and the sulphuric acid recovered from the acidified liquids as barium sulphate.

Heat the solution of sodium sulphate to boiling, precipitate with a slight excess of barium chloride, and allow the precipitate to settle twenty-four hours, unless the results are desired at once, in which case the precipitation may be completed inside of three hours, by keeping the liquid at a temperature not less than 75° C. during that time.

The acids and distilled water, used in the analysis, should be measured, and a blank analysis carefully made by evaporating with the pure soda, and the trace of barium sulphate deducted

from that of the analysis proper. Exp. 20-22 are three comparative analyses from the writer's note-book.

TABLE VI.  
COPPER ANALYSIS.

		Per cent. sulphur.		Per cent. sulphur.
20	Direct precipitation	0.0000	Author's method	0.0023
21	" "	0.6000	" "	0.6500
22	" "	0 to 0.0050	" "	(1) 0.0112
22	Chlorine method	0.0189?	" "	(2) 0.0094

It is evident that the method just detailed, is extremely well adapted to the analysis of refined copper.

The sulphur in the metal is brought into solution, and finally precipitated in a pure condition without loss, and a blank analysis is possible under the same conditions. The difference between the two results, expresses the true quantity of sulphur present.

Another chemist stated sometime ago that he, also, had been obliged to try a similar plan. The author has, however, worked out the foregoing process in its improved form independently, and in presenting this standard method, desires to express his indebtedness to the gentleman who has so kindly consented to read the paper before the assembly.

## ACIDIMETRIC ESTIMATION OF VEGETABLE ALKALOIDS. A STUDY OF INDICATORS.<sup>1</sup>

BY LYMAN F. KEBLER.

Received September 9, 1895.

THE titration of alkaloids with volumetric acid solutions has been evolved from the study of the basicity of the alkaloids on the one hand, and from their behavior with indicators on the other. The method appears to have been developed somewhat spasmodically from quite an early period. As early as 1846 M. Schlössing<sup>2</sup> proposed the method and applied it to the titration of nicotine with a view of establishing its equivalent; using sulphuric acid and litmus in his work. Sixteen

<sup>1</sup> Read at the Springfield meeting.

<sup>2</sup> 1847, *Comp. rend.*, 23, 1142; 1847, *Ann. Chim. Phys.* [3], 19, 230; *Chem. Gaz.*, 5, 41; *Am. J. Pharm.*, 19, 68.

years later the work was taken up by Wittstein,<sup>1</sup> who was followed by F. M. Brandl,<sup>2</sup> Liecke,<sup>3</sup> Kosutany,<sup>4</sup> and G. Dragen-dorff.<sup>5</sup> Up to this time nicotine and conine were the only alkaloids operated on, and litmus the only indicator employed. In 1879 L. van Itallie<sup>6</sup> extended the work to several other alkaloids, using lacmöld as indicator. A. W. Gerrard<sup>7</sup> a few years later employed litmus and phenolphthalein in titrating the alkaloids of belladonna. From the contributions of O. Schweissinger,<sup>8</sup> who used cochineal as indicator, and those of E. Dieterich<sup>9</sup> and P. C. Plugge<sup>10</sup> we may ascribe the impetus which the titration of alkaloids with volumetric acid solutions received at the beginning of the present decade.

The method had been gaining ground rapidly when several most valuable communications appeared by C. C. Keller,<sup>11</sup> of Zürich, since which great improvement has been made.

In volumetric analysis, the first question demanding attention is a suitable indicator or delicate end reaction.<sup>12</sup> The object of this communication is to present the results of a study of five indicators in titrating alkaloids, thinking perhaps it may be of some service in formulating systematized methods of analysis in alkaloidal chemistry. The discordant results of analysis often obtained by different chemists operating on the same sample are greatly to be regretted. It is the writer's opinion that

<sup>1</sup> 1862, *Vierjahrschr. prakt. Pharm.*, 11, 351.

<sup>2</sup> 1864, *Vierjahrschr. prakt. Pharm.*, 13, 322.

<sup>3</sup> 1865, *Mittheilungen des hannov. Gew.-Ver.*, p. 160; *Ding. poly. J.*, 178, 235; *Polyt. Notizbl.*, No. 20; *Ztschr. anal. Chem.*, 4, 492.

<sup>4</sup> 1873, Kosutany, *Anal. Bestim. einiger Bestandth. d. Tabakspflanze*. Diss. Altenburg, Hungary.

<sup>5</sup> 1874, *Chem. Werthbestim.*, p. 42 and 55; see also *Plant Analyses*, 1884, Eng. Ed., pages 63 and 188.

<sup>6</sup> 1879, *Nederland. Tydschr. v. Pharm.*, Jan; *Analyst*, 14, 118.

<sup>7</sup> 1882 and 1884, *Year-Book of Pharm.*, p. 401, 447.

<sup>8</sup> 1886, *Pharm. Centralhalle*, 27, 492.

<sup>9</sup> 1887, *Pharm. Centralhalle*, 28, 21; *Pharm. J. Trans.* [3], 17, 888; *Am. J. Pharm.*, 59, 179.

<sup>10</sup> 1887, *Arch. d. Pharm.* [3], 25, 45, 49; *J. de Pharm. et de Chim.* [5], 15, 571; *Ber. d. chem. Ges.*, 20, 148; *J. Chem. Soc.*, 52, 621.

<sup>11</sup> 1892, *Schweiz., Wochenschr. f. Chem. u. Pharm.*, 30, 501, 509; *Am. J. Pharm.*, 65, 78. 1883, *Schweiz., Wochenschr. f. Chem. u. Pharm.*, 31, 473; *Ztschr. Oesterreich-Apoteker.*, 47, 563, 586; *Am. J. Pharm.*, 66, 42.

<sup>12</sup> Alkaloids, generally, are neutral to phenolphthalein, consequently it cannot be employed in titrating alkaloids directly. It is available for indirect titrations, i. e., estimating the amount of acids combined with an alkaloid in its neutral salts.

the discrepancies are chiefly due to differences in *modus operandi*, to defective apparatus, and, in volumetric analysis, to different end reaction tints arbitrarily assumed by each worker.

In order to eliminate the factors of uncertainty as completely as possible the methods of operation were carefully written out and closely adhered to in all the work. The burettes and a pipette were carefully calibrated in order to ascertain the necessary factor for correction. The method of calibration was as follows: each burette and pipette was exactly filled to the zero mark with distilled water, at 15° C. and ten cc., delivered into a tared weighing flask and weighed, then the next ten cc. were treated in the same manner, and so on until the entire capacity of each was tested. A glass-stoppered cylinder was also standardized. All efforts to standardize a liter flask were thwarted. A large balance sufficiently sensitive to do the work satisfactorily could not be found.

In titration the personal equation plays an important part. Authorities are not agreed on end reaction tints, each operator relying on his own judgment. The writer thinks it correct to titrate to the point where a different color from the initial color is developed. In order to obtain standard end reaction tints for alkaloids it will be necessary to prepare some absolutely pure alkaloid; treat a molecular quantity of the alkaloid with an equivalent of the acid in question to form a neutral salt, then add one drop more of the decinormal acid for an acid color reaction. For alkaline tints add one drop of the centinormal alkaline solution to a solution of neutral alkaloidal salt, theoretically prepared.

In this work the writer titrated from acid to alkaline solutions as follows: Brazil wood, from yellow to onion-red, the purple ultimately fading to this; cochineal from yellow to bluish-red; haematoxylin from yellow to brown-orange; litmus from red to onion-red, and methyl orange from red to straw-yellow.

The indicator solutions were prepared according to the most approved processes. Cochineal and litmus were prepared according to the specifications of Sutton's Volumetric Analysis, sixth edition. Phenolphthalein, one gram dissolved in one liter of fifty per cent. alcohol. Haematoxylin, well crystallized, one

gram dissolved in 100 cc. of strong alcohol. The method best suited for preparing the Brazil wood solution, is to place three grams of the wood into a casserole, add ten cc. of distilled water, boil gently for a few minutes, cool, and filter. A freshly prepared solution has given the writer the most satisfactory results. Methyl orange, one gram dissolved in one liter of distilled water. Considerable difficulty was experienced in obtaining even a fairly satisfactory product of methyl orange. The method proposed by Mr. B. Reinitzer<sup>1</sup> for preparing the litmus solution did not come to the writer's notice until considerable work had been done with the solution prepared as above.

In titration the following quantities of the several indicators were employed: methyl orange, Brazil wood, cochineal, and phenolphthalein, five drops each; litmus ten drops and haematoxylin three drops.

The standard solution employed in this investigation, from which the exact strength of the other volumetric solution was determined, was a solution of normal sulphuric acid. This solution was prepared from data obtained by the several methods; titration against pure anhydrous sodium carbonate, using the above indicators; precipitation as barium sulphate and Weinig's<sup>2</sup> process. After some experimentation, it was found that Weinig's method gave the most satisfactory results. The method is simple and yields very concordant results. The following are the data obtained from an approximately normal sulphuric acid solution with the above methods:

Indicators, and methods.	No. of cc. of acid solution required per ten cc. of normal sodium carbonate.	Grams of SO <sub>3</sub> in ten cc. of the acid solution.
Brazil wood.....	9.50	0.4211
Haematoxylin.....	9.54	0.4192
Cochineal.....	9.50	0.4211
Litmus.....	9.50	0.4211
Methyl orange.....	9.50	0.4211
Phenolphthalein.....	9.45	0.4216
Weinig's method.....	....	0.4247
Barium sulphate method..	....	0.4200

Due precaution was taken to boil the solution thoroughly with

<sup>1</sup> 1894, *Ztschr. angew. Chem.*, 547, 573; *Chem. News*, 70, 225, 239, 249.

<sup>2</sup> 1892, *Ztschr. angew. Chem.*, 204; *Analyst*, 17, 99.

the indicators requiring it. With solutions of the above strength it was impossible to detect any difference in the sensitiveness of most of the indicators.

With the normal sulphuric acid solution a normal solution of pure potassium hydroxide was standardized. From the normal sulphuric acid solution and normal alkaline solution there were prepared, respectively, a decinormal acid solution and a centinormal alkaline solution. The two solutions thus prepared were carefully titrated against each other, employing the above indicators with the following results :

Indicators.	No. of cc. of normal sulphuric acid.	No. of cc. of centinormal KOH required per ten cc. of deci- normal $\text{H}_2\text{SO}_4$ .	
		LaWall.	Kebler.
Phenolphthalein.....	10	101.80	102.00
Brazil wood.....	10	99.56	100.00
Cochineal.....	10	100.58	99.80
Haematoxylin .....	10	99.76	100.00
Litmus .....	10	99.97	99.60
Methyl orange .....	10	92.67	98.53

My associate, Mr. LaWall, took up a portion of the work, which he executed independently, using, however, the same solutions and apparatus that the writer employed. The above, and all subsequent results, are the average of duplicate, triplicate or more titrations.

The titration of pure alkaloids, as found in the market, was next undertaken. With quinine and codeine the following method was used: two grams of the alkaloid were placed in the cylinder, dissolved in alcohol, and diluted up to 100 cc. with alcohol. To ten cc. of this solution and the requisite quantity of indicator contained in a suitable beaker, the decinormal acid solution was added to slight excess, agitated, allowed to stand a few minutes, the sides of the beaker well washed down with distilled water, adding about forty cc., and the excess of acid titrated back with the centinormal alkaline solution.

With alkaloids not freely soluble in alcohol, the following procedure was adopted: two grams of the alkaloid were placed into a 200 cc. beaker, seventy-five cc. of decinormal acid added, the contents of the beaker warmed on a water-bath and occasionally agitated until the alkaloid was dissolved. The beaker



and contents were then cooled, the contents transferred to a 100 cc. cylinder, the beaker carefully rinsed with several successive portions of water, transferred to the 100 cc. cylinder and finally made up to 100 cc. with water. Each ten cc. contained two-tenths of a gram of alkaloid and seven and a half cc. of decinormal acid solution. After adding the requisite amount of indicator to ten cc. of the alkaloidal solution and diluting up to about fifty cc., the excess of acid was carefully retitrated. Two or more titrations were made in every case, with the same solution and indicator, by adding to the solution just finished, another portion of the decinormal acid solution and retitrating with the centinormal alkaline solution, taking finally the average reading.

The above methods of titration and preparation of solutions were employed with several pure alkaloids. The results are tabulated below.

Indicators.	Quinine.		Strychnine.		Morphine.		Codeine.	
	LaWall.	Kebler.	Kebler.	Kebler.	Kebler.	Kebler.	Kebler.	Kebler.
Brazil wood.....	99.90	101.97	99.36	98.93	95.75			
Cochineal .....	105.56	102.54	103.20	99.08	97.09			
Haematoxylin .....	99.81	103.37	100.03	98.17	95.90			
Litmus .....	101.80	103.55	103.54	98.93	96.38			
Methyl orange.....	....	123.27	104.21	100.59	98.11			

The number of times the analyst is requested to investigate the purity of refined alkaloids is comparatively small, but the crude alkaloids claim a greater share of his time and attention.

The next step was to investigate the adaptability of the above process to crude morphine and crude cocaine. The results are as follows:

Indicators.	Crude morphine.		Crude cocaine.	
	LaWall.	Kebler.	Kebler.	Kebler.
Brazil wood.....	99.23	98.47	95.90	
Cochineal.....	100.14	99.53	97.11	
Haematoxylin .....	99.08	97.59	95.74	
Litmus .....	99.50	98.93	96.82	
Methyl orange.....	102.10	100.02	100.14	

With the same crude morphine the ash method yielded 97.59 per cent., the lime-water method 98.22 per cent., and the absolute alcohol method 98.33 per cent. of pure morphine.

A complete analysis was made of the crude cocaine to ascer-

tain how nearly the titrations corresponded with the gravimetric process of Dr. Squibb.<sup>1</sup>

	Per cent.
Moisture .....	0.405
Cocaine nearly pure .....	97.300
Material soluble in ether .....	0.100
Material insoluble in ether .....	1.810
Loss .....	0.385
Total.....	100.00

Notwithstanding the fact that crude alkaloids claim considerable attention on the part of the analyst, yet only a few are found already extracted on the market. It generally happens that the operator is requested not only to determine the amount of pure alkaloids, but also to extract them from their natural sources. For this purpose the writer employed a modification of Keller's process. The method is as follows: place ten grams of the dry drug into a 250 cc. flask, add twenty-five grams of chloroform, seventy-five grams of ether, stopper the flask securely, agitate well for several minutes, add ten grams of ten per cent. ammonia water, then agitate frequently and during one hour. On adding five grams more of ten per cent. ammonia water and shaking well, the suspended powder agglutinates into a lump, the liquid becomes clear, after standing a few minutes, and can be poured off almost completely.

1. When the mixture has completely separated, pour off fifty grams into a beaker, evaporate the solvent on a water-bath, add ten cc. of ether, and evaporate again. Dissolve the varnish-like residue in fifteen cc. of alcohol, with heat, add water to slight permanent turbidity, the requisite quantity of indicator and an excess of the acid solution; retitrate with the centinormal alkaline solution.

2. When the mixture has completely separated pour fifty grams into a separatory funnel, treat at once with twenty cc. of acidulated water. After thorough agitation and complete separation remove the aqueous solution into a second separatory funnel. Repeat the above operation twice more successively with fifteen cc. of slightly acidulated water. The acidulated water

<sup>1</sup> Ephemeris, 3, 1171.

in the second separatory funnel is rendered alkaline with ammonia water, the alkaloid removed successively with twenty cc., fifteen cc., and fifteen cc. of a mixture of three parts (by volume) of chloroform and one part of ether. Collect the chloroform-ether mixture in a tared beaker and distil off the solvent. The varnish-like residue is twice treated with eight cc. of ether, evaporated on a water-bath and dried to constant weight on the water-bath. The varnish-like residue is next dissolved in fifteen cc. of alcohol and treated as in (1) above.

Nux vomica and ipecac root were treated according to processes (1) and (2); belladonna leaves according to process (2). The results are as follows:

	Per cent. of alkaloids in nux vomica by process (1).		Per cent. of alkaloids in nux vomica by process (2). Gravimetrically.		Per cent. of alkaloids in nux vomica by process (2). Volumetrically.		Per cent. of alkaloid in ipecac root by process (1.)	
	LaWall.	Kebler.	LaWall.	Kebler.	LaWall.	Kebler.	LaWall.	Kebler.
Brazil wood.....	2.04	2.58	2.94	3.00	2.37	2.37	2.46	2.54
Cochineal .....	2.64	2.69	2.86	3.10	2.42	2.39	2.59	2.49
Haematoxylin ...	2.18	2.24	2.88	3.11	2.23	2.27	2.48	2.54
Litmus .....	2.38	2.34	2.93	3.05	2.55	2.37	2.55	2.57
Methyl orange...	3.02	3.64	2.93	3.02	2.65	2.61	2.95	3.30

	Per cent. of alkaloid in ipecac root by process (2). Gravimetrically.		Per cent. of alkaloid in ipecac root by process (2). Volumetrically.		Per cent. of alkaloids in belladonna leaves by process (2). Gravimetrically.		Per cent. of alkaloids in belladonna leaves by process (2). Volumetrically.	
	LaWall.	Kebler.	LaWall.	Kebler.	LaWall.	Kebler.	LaWall.	Kebler.
Brazil wood.....	2.58	2.60	2.36	2.35	0.26	0.20	0.19	0.15
Cochineal .....	2.63	2.68	2.52	2.33	0.28	0.20	0.24	0.14
Haematoxylin ...	2.58	2.68	2.35	2.33	0.27	0.22	0.21	0.13
Litmus .....	2.62	2.60	2.40	2.25	0.24	0.18	0.20	0.15
Methyl orange...	2.66	2.63	2.89	2.61	0.25	0.20	0.23	0.20

According to the well-established method of Messrs. Dunstan<sup>1</sup> and Short, the nux vomica examined contained 2.89 per cent. of crude alkaloid. On carefully titrating this crude product with a volumetric acid solution, 2.12 per cent. of pure alkaloid was indicated. Cochineal was used as an indicator. These figures show that this method produces an alkaloid residue containing a smaller percentage of pure alkaloid than that obtained by Keller's process.

<sup>1</sup> 1883, Pharm. J. Trans. [3], 13, 665.

From the results embodied in this paper it can safely be concluded that methyl orange cannot be numbered with the indicators suitable for titrating alkaloids. With centinormal, fifth decinormal and other solutions of various strengths it fails to give satisfactory results. Notwithstanding the sensitiveness claimed for it, the writer believes that its days, as an ideal indicator, are numbered. Even Professor Lunge, the staunch advocate of methyl orange, has admitted that a properly prepared solution of litmus is quite superior to this indicator, in inorganic estimations.

A solution of litmus prepared according to the directions herein employed is quite unsatisfactory for delicate titrations. The method proposed by Reinitzer promises to be better suited.

Of the indicators thus far considered, haematoxylin, Brazil wood, and cochineal give very promising results. Haematoxylin justly claims first place and Brazil wood the second. Other indicators will be considered in due time.

As stated above, the prime object of this investigation is to ascertain what indicators are best adapted to the titration of alkaloids; but in order to determine how reliable the results were, gravimetric determinations necessarily formed a part of the work.

When it is remembered that not only do analytical methods contain inherent limitations, but also that each operator possesses a positive or a negative equation of error, the reader will undoubtedly concur with the writer that the results are very satisfactory. Attention must again be called to the fact that the work was conducted under precisely the same conditions.

As would naturally be expected, the amount of alkaloid obtained by process (2) is smaller than that secured by process (1). A small per cent. of the alkaloid may be lost during the process of extraction. The small amount of coloring-matter possibly vitiates the results, or perhaps some non-alkaloidal substance increases the yield in process (2).

From the hundreds of assays made by the author, he feels justified in stating that all of the gravimetric processes yield products containing considerable non-alkaloidal matter, and hopes that the day is not far distant when all gravimetric results

will at least be supplemented by volumetric methods, if not displaced by them.

THE MORE VALUABLE LITERATURE ON INDICATORS DURING THE LAST TWO DECADES.

1877. B. Luck: *Ztschr. anal. Chem.*, 16, 332.  
 1880. A. Baeyer: *Ann. Chem. (Liebig)* 202, 68.  
 1881. R. B. Warder: *Am. Chem. J.*, 3, 55.  
 1882. G. Tobias: *Ber. d. chem. Ges.*, 15, 2452.  
 1883. R. T. Thomson: *Proc. Phil. Soc., Glasgow*, 14, 56, 173; *Chem. News.*, 47, 123, 135, 184.  
 1883. H. Beckurts: *Pharm. Centralhalle*, 24, 333; *Abstr., Ber. d. chem. Ges.*, 17, 3073.  
 1883. J. Wieland: *Ber. d. chem. Ges.*, 16, 1989.  
 1883. R. T. Thomson: *Proc. Phil. Soc. Glasgow*, 15, 63, 194; (1884) *Chem. News*, 49, 32, 38, and 119.  
 1884. H. Beckurts: *Pharm. Centralhalle*, 25, 101; *Abstr., Ber. d. chem. Ges.*, 17, 238.  
 1884. C. Kraemer: *Ber. d. chem. Ges.*, 17, 1875.  
 1884. F. A. Flückiger: *Arch. d. Pharm. [3]*, 22, 605.  
 1885. G. Lunge: *Ber. d. chem. Ges.*, 18, 3290.  
 1885. R. T. Thomson: *Chem. News*, 52, 18, 29.  
 1885. M. Berthelot: *Comp. rend.*, 100, 207; *Abstr., Ber. d. chem. Ges.*, 18, 93.  
 1885. M. C. Traub: *Arch. d. Pharm. [3]*, 23, 27; *Abstr., Ber. d. chem. Ges.*, 18, 126.  
 1885. M. Dechan: *Pharm. J. Trans. [3]*, 15, 849.  
 1885. J. H. Long: *Chem. News*, 51, 160.  
 1885. H. N. Draper: *Chem. News*, 51, 206.  
 1885. R. Engle and J. Ville: *Bull. Soc. Chim.*, 44, 17.  
 1885. B. Fischer and O. Philipp: *Arch. d. Pharm. [3]*, 23, 434; *Abstr., Ber. d. chem. Ges.*, 18, 583.  
 1885. T. Lehmann and J. Petri: *Arch. d. Pharm.*, [3], 23, 243; *Abstr., Ber. d. chem. Ges.*, 18, 625.  
 1889. J. H. Long: *Am. Chem. J.*, 11, 84.  
 1891. A. H. Allen: *Analyst*, 17, 186, 215.  
 1891. G. Lunge: *J. Soc. Chem. Ind.*, 10, 314.  
 1891. J. Lüttke: *Apoth. Ztg.*, 7, 643; *Ztschr. anal. Chem.*, 31, 692.  
 1893. M. B. Breed: *J. Frank. Inst.*, 135, 312; *J. Anal. Appl. Chem.*, 7, 204.  
 1893. R. T. Thomson: *J. Soc. Chem., Ind.*, 12, 432.  
 1894. B. Reinitzer: *Ztschr. angew. Chem.*, 547, 573; *Chem. News*, 70, 225, 239, 249.  
 1894. G. Lunge: *Ztschr. angew. Chem.*, 733.  
 1894. W. Schafer: *Apoth. Ztg.*, 9, 839; *Abstr., Analyst*, 20, 37 (1895).

## NEW BOOKS.

ELEMENTS OF MODERN CHEMISTRY. BY CHARLES ADOLPHE WURTZ.  
Fifth American Edition. Revised and enlarged by Wm. H. Greene,  
M.D., and Harry F. Keller, Ph.D. 12 mo. pp. 788. Philadelphia: J.  
B. Lippincott & Co., 1895.

On the whole, this is a very good text-book, well adapted to the needs of high schools and general use in colleges, as its popularity proves. From the reviewer's standpoint, however, it possesses two distinct faults. First, the disproportionately large space given to organic chemistry. This part of the subject is full of very important information, but it has taken on too much of the style of a dictionary and too little of the analytical method of a treatise. The result is 360 pages of material which by judicious generalization should have been condensed to half that amount, in order to correspond in size to the rest of the book. For instance, two pages are given to describing succinic acid, and yet, barely a single page each to barium, strontium or cadmium, with all their compounds; the derivatives of urea take five pages, while the subject of chemical energy and thermochemistry is disposed of in just half that space. Secondly, the lack of true inductive reasoning in establishing the probability of the atomic theory. The introductory pages on chemical theories and laws contain the "Articles of Faith" of the atomic theory, very clearly stated, but it must be said that the theory itself is virtually taken for granted. For instance, speaking of forming ferrous sulphide by melting iron filings and sulphur together, it is said, "After cooling it is perfectly homogeneous, neither iron nor sulphur can be recognized. Both have disappeared as such." This is perfectly true, and according to experience. But, a few lines further we have: "It cannot be admitted that these two substances are confounded in the molecule, or that the effect of the combination of sulphur with iron is an interpenetration of the two bodies, so intimate that they both disappear in what might be called a homogeneous mixture." The student might very naturally inquire why it could not be admitted, since such an admission would coincide so well with the facts as far as we know them; and the only answer that

could be made would be, "It would not agree with the atomic theory." The student might well say, "So much the worse for the theory!"

We note the absence of thermochemical data, the most important of which might well serve for illustrating the general relations of the elements to each other and to the acids. In the chapters describing the metals and their compounds, many of the simple blowpipe tests for identifying the elements are omitted, and for some common elements no qualitative tests at all are given. The table of the melting-points of the metals needs revision. The electrolytic method of refining copper cannot now be spoken of as expensive. The mineral Edisonite, spoken of as a form of titanite oxide, has been proved to be rutile. Among the methods of manufacturing caustic soda, bleaching powder, and potassium chlorate, the electrolytic methods are not mentioned—as they surely should be.

On the other hand, the numerous revisions to which the text has been subjected have ensured the almost certain accuracy of the facts presented and the absence of mistakes. The revision up to date has been done in a way which reflects great credit on the revisers. Granted that the teacher will remedy the faults first spoken of by cutting down much of the detail of the organic chemistry and presenting the atomic theory in a more logical manner, and we may pronounce the book the best elementary text-book of chemistry of the year.

JOSEPH W. RICHARDS.

JUSTUS VON LIEBIG, HIS LIFE AND WORK. BY W. A. SHENSTONE. 12mo. pp. 219. \$1.25. New York: Macmillan & Co.

Liebig's personality was an interesting one. His life was one of earnest purpose and hard work. He was a many-sided man, and his influence was felt in many directions. In investigation, as a man of affairs and as a popular teacher, Liebig's work has been of use to his kind. Of the brilliant chemists of his day—Graham, Dalton, Wöhler and Dumas, among others—his career is the most interesting. Liebig's work began in Gay Lussac's laboratory where in connection with his work on the fulminates he discovered isomerism. In 1824 he went to Giessen, and in 1852 to Munich. "Liebig was essentially a pioneer in science.

In the course of his life he took the lead in no less than four great departures. The first was in organic chemistry, the second and third in the application of chemistry to agriculture and physiology, the fourth \* \* was the outcome of his labors as a teacher. His work, like that of other pioneers was, of course, not always correct in all points of detail. But it had all the greater merits of good pioneering work in a most marked degree. It almost always pointed the right way, and its remarkable influence in determining the direction of subsequent research has been singularly permanent." To this may be added that he was a virile man, vigorous and trenchant in debate, but honoring truth above all things, and willing to acknowledge his errors—and several times he was in the wrong.

Professor Shenstone has given us a very interesting and lucid account of his life and his work.

E. H.

---

NOTE.

*Determination of Acetic Acid in Vinegar.*—Dr. B. F. Davenport wishes to call attention to his article on this subject printed in the *Journal of Analytical Chemistry*, 1, 4, in view of the fact that Prof. Leeds' attention had apparently not been called to it before writing the article printed in the September number of this journal, p. 741.



# THE JOURNAL

OF THE

## AMERICAN CHEMICAL SOCIETY.

---

### AN ELECTROLYTIC PROCESS FOR THE MANUFACTURE OF WHITE LEAD.<sup>1</sup>

By R. P. WILLIAMS.

Received September 9, 1895.

WHITE LEAD is the basis *par excellence* of white paint. For hundreds of years it has been used, mixed with linseed oil, as the main pigment where permanent, opaque, white color is desired.

Up to the present time there have been but two radically different processes of manufacture that have proved in any degree successful. These are known as the Dutch and the French processes. The English and the German are only modifications of the same principle as the others. The Dutch process is the only really successful one. I do not propose to go into the details of either of these processes, since they are well known to every chemist, but only to recall just enough of them to serve as the basis of comparison and as an introduction to the one I am to describe. Both the French and the Dutch, as well as the many modifications of them, depend upon one compound; *viz.*, lead acetate (or better, sub-acetate). This is the compound which has always been regarded as the essential first step in white lead manufacture. The fact is interesting, since white lead as a pigment has been known for more than 2,000 years, and from the earliest times it has been made by the action of acetic acid on lead. The name, Dutch process, is a

<sup>1</sup> Read at the Springfield meeting.

misnomer, as the process was introduced by the Dutch or Flemish people over 300 years ago from Italy, where it had been employed for hundreds of years previously. In fact, Pliny in the first century describes the essentials of the process, and it is said to have been employed in his country ever since his time, though, of course, on an extremely limited scale at first. Indeed Theophrastus, about 300 B. C., describes the preparation of a white pigment from lead and vinegar. This may have been the acetate, or it may have been the carbonate. The new process is a radical departure from all the old ones in not employing acetic acid at all, but in acting upon lead with nitric acid, which is generated by electricity.

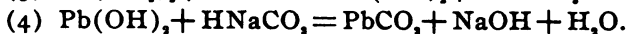
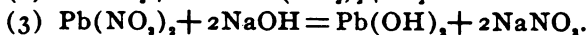
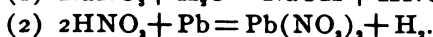
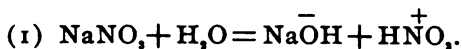
The process consists of four reactions, as given below. First, the electrical preparation of nitric acid and sodium hydroxide. Second, the action of the nitric acid on lead, forming lead nitrate. Third, the reaction of lead nitrate and sodium hydroxide to form lead hydroxide. Fourth, the combination of lead hydroxide and sodium bicarbonate to form lead carbonate.

In the first step of the process, a solution of sodium nitrate is decomposed by an electric current from a dynamo. The strength of solution required is not important, 10° Baumé, or say one pound to the gallon, being sufficient. This solution is put into a series of cells, constructed of wood, and divided into two compartments by a porous partition. At the plus electrode is fastened a pig of lead, and at the minus a sheet of copper. The solution being run in from an overhead reservoir, and the current turned on, the nitrate is decomposed according to equation (1), nitric acid collecting at the plus electrode and sodium hydroxide at the minus. The nitric acid at once attacks the lead and forms lead nitrate, which dissolves, equation (2), whereas the sodium hydroxide produces no effect on the copper at the negative pole. Finally the lead nitrate solution and the sodium hydroxide solution are drawn off separately, and mixed as desired, in quantitative proportions, in a receptacle. The result as shown in equation (3), gives lead hydroxide as a white, amorphous precipitate, and leaves sodium nitrate in solution. This is practically the original nitrate, and its regeneration shows one of the economic excellencies of the

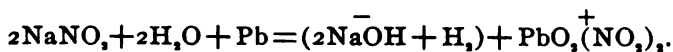
process, for the nitrate can be used over and over again, as the source of more acid.

It has been found at the experiment station, that but little additional sodium nitrate is required for a repetition of the process as complete as the original. The lead hydroxide is then filtered from the sodium nitrate. This is done automatically and continuously, by a rotary filtering device, and the sodium nitrate is pumped back into the original reservoir. The fourth step is, in some respects, the most interesting of all, and consists in adding to the lead hydroxide a solution of sodium bicarbonate (or of the normal carbonate). Reaction (4) at once takes place. It will be noted that sodium hydroxide is the product in solution, and lead carbonate the precipitate. Another beauty of this process is that the sodium hydroxide removes most of the impurities, if there are any, in the lead hydroxide; for instance, it will dissolve any salts of aluminum or of zinc, and it removes organic matter.

These impurities appear in the solution, leaving the precipitate remarkably white. Once more, this by-product, sodium hydroxide, by passing carbon dioxide into it, is converted into bicarbonate and the latter can be used again. Thus the main agent in each of the two principal steps, sodium nitrate and sodium bicarbonate, is made to do duty over and over again, with but slight additions.



It is doubtful whether (1) and (2) take place as above, but probably the reaction is as follows, since hydrogen is liberated at the minus electrode :



Let us now turn from the theoretical to the practical part of the matter. The first question which naturally arises is, will this process so beautiful in theory, and as a laboratory experiment, work on a large scale and give sufficiently practical

results to compete with the other methods of manufacture, and make it a lasting contribution to inventive science?

An experimental station was for several months in operation in Cambridge, Mass., erected and run under the direction of Mr. Arthur Benjamin Brown, the inventor of the process. This was capable of turning out some 500 pounds of white lead per day. Its success was regarded as beyond question. The cost of white lead by this process is more than covered by the gain in weight, and is but a fraction of the cost by the Dutch method. The reasons are, first, in the electrolytic process pig lead is used, as it comes from the smelting furnace. In the Dutch it has to be remelted, cast into "buckles" of definite size, and, after the action of acetic acid, from one-third to one-half is left uncorroded and has to be recast.

Second, the process is almost instantaneous, as every reaction takes place rapidly, while by the other mode from two to six months is required.

Third, in materials and labor there is great saving. No free acid is used, either acetic or nitric, and the agents sodium nitrate and bicarbonate, are used repeatedly. By the old method a plant covering a large area is filled for months with fermenting tan bark or manure, acetic acid and lead, while the process is going on, and at its completion, the product is removed with much labor, and has to be thoroughly and repeatedly washed to dissolve out any lead acetate remaining. It must be ground and reground under water, and even then is not likely to be of uniform texture. It is also a poisonous and dirty process. The electric method being continuous, is complete the same day, requires but a very small force of men, as almost all the operations are automatic, and is a clean and non-poisonous process.

The texture of the product is almost molecular in fineness, as might be expected from its being produced by replacement in the hydroxide. Hence it needs no grinding. It is so fine as to remain suspended in water for a long time, and in order to filter it a special brand of cloth had to be made, as even filter-paper would scarcely retain it.

One of the most important practical questions is: How does

paint made from electrolytic white lead compare with that made from Dutch lead in durability, opacity, and covering power? Specimens have been submitted to some of the largest dealers and painters in New England and elsewhere, and Mr. Brown, the inventor, has spent the last two years, aided by a competent corps of assistants, not only in the development of his new process, but in making thorough and systematic tests of the product. Inside and outside surfaces have been exposed to the severest extremes of weather, to the varied fumes of the laboratory, and to other crucial tests. Dutch paint and electrolytic paint have been exposed side by side for two years, and no difference can be detected in durability or opacity. The covering power of the new paint is considerably greater than that of the Dutch. Experiments vary as to the increased percentage from twelve to twenty, or even higher, but in no case was there found to be a smaller percentage.

What is the cause of such an increase? This leads us to discuss somewhat more fully the nature and composition of white lead made by the various processes. Dutch white lead consists approximately of two molecules of the carbonate to one of the hydroxide,  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ . This, however, appears not to be constant, as might be inferred from its mode of manufacture. Lead hydroxide is a white, amorphous substance. Lead carbonate is either a spongy transparent, globular powder, or is crystalline. Whether globular or crystalline depends upon its mode of preparation. Now certain properties of these two forms are quite different, and this difference explains the use of one and the disuse of the other form as a pigment. The globules of the one form are said to be from 0.00001 to 0.00004 of an inch in diameter. These, in the grinding of lead with linseed oil, are supposed to take up the oil, somewhat as a sponge absorbs water. The Dutch process lead is the globular variety, and to this fact has been attributed the greater body and permanence of the paint made from it than that made by most other processes. The crystalline variety of the carbonate is found not to absorb oil to anything like the same extent as the globular, no matter to what degree of fineness it is ground, the surface of the minute crystals being impervious. Half a century ago Thenard

invented the "quick process lead," or "French process." This is now carried on in Clichy, France, and some other places, and sold as "Clichy White." It is made by dissolving litharge in acetic acid and then passing into the sub-acetate of lead solution formed, carbonic acid gas. Thus is formed neutral lead carbonate. It was at first thought to be a revolutionary process, but it soon became apparent that the product did not give the capacity or body, which Dutch lead gave, and of course it lacked permanence. Made in this way the carbonate is crystalline. Under the brush it is found not to cover as much surface and not to spread as well, or it is said to lack "body," although of the same composition as the other. Other rapid processes—and there have been hosts of them—have invariably met with no better success, for the reason that the carbonate formed is the crystalline instead of the globular variety. To this fact we may mainly attribute the long continued use of Dutch process lead. The committee of experts appointed by the British Home Secretary, visited forty-six works, and found only one using the precipitation process and three the chamber process. They say: "While some of the substitutes are cheaper to make, and far less poisonous, yet they are far from equalling the Dutch lead as a pigment. Neither can they recommend other process than the old Dutch process, for manufacturing the product."

Thus we see that until now, no cheaper method has been found for producing the globular variety. The electrolytic process *does* produce the globular kind, and a finer variety even than the Dutch, so fine in fact, that it was almost impossible to find a filter that would retain it. This probably accounts for the superiority of the electrolytic brand, as regards body and covering power over any other kind produced. Experiment shows that the pure carbonate will do as well as a mixture of carbonate and hydroxide. By the new process it is easy to make either the pure carbonate, or a mixture in any proportion, of carbonate and hydroxide. The practicability and cheapness of the electrolytic process, and the efficiency of the product being conceded, we may inquire lastly: What are the probabilities of this method being superseded by others in the future?

No other white pigment has yet been formed, or seems likely to be found, which will take the place of white lead. The two main substitutes are zinc white,  $\text{ZnO}$ , and permanent white,  $\text{BaSO}_4$ . But these do not stand the test with lead white, having far less capacity, and less covering power. Especially will they not compete with the cheapening of the latter by the new process. Hence, we must look to lead to give us the white pigment of the future.

Now what are the possible ways of making lead carbonate? There are but three common solvents of the metal; chlorine, acetic acid, nitric acid. Chlorine is at once ruled out for all practical purposes, for reasons that need not be mentioned here. Acetic acid seems to have been the substance universally employed to the present time, for getting the metals into a preliminary state for making the carbonate. As before noted, from the time of Theophrastus to the present day a host of persons in every age and many countries, have experimented and written upon the subject, all using the same method so far as concerns making lead acetate.

The inventor of the present process, worked a long time upon the acetate, but as acetic acid is an organic substance of quite complex structure, it broke up very readily under influence of an electric current, giving rise to unendurable fumes, and its use had to be abandoned. For these reasons it is safe to say that no electrolytic process is likely to employ the lead acetates. The only solvent left is therefore nitric acid. Free nitric is not likely to be used for three reasons: First, it could hardly be employed in electrolysis; Second, it would be more expensive than Chile saltpeter; Third, its reaction with lead would give rise to noxious nitric oxide fumes, and its by-product would not be re-usable. It should be said that no gases except hydrogen arise in the electrolytic process, in which the acid, as fast as liberated, combines with the lead, as may be seen from equation (2).

Now the only feasible source of nitric acid yet found, is either sodium or potassium nitrate. The former being far the more abundant and cheaper, is here as elsewhere employed, as a source of the acid, and no other nitrates are found to any extent in nature.

It would seem from what has been set forth, that not only is the process above described the most valuable and revolutionary ever invented for the manufacture of white lead, but that there is not a probability of any other process taking its place, in the near future.

This new process was invented in 1892, by Arthur Benjamin Brown, a chemist and mining engineer of Boston. It is to-day for the first time made public. The reason this has not before been done is because time was necessary to complete many details for production on a large scale, and to secure requisite patents. These are now completed, and a large company is organized to put the process into practical operation. I propose for this invention the name—The Brown Electrolytic Process.

### THE CHLORIDES OF ZIRCONIUM.<sup>1</sup>

By F. P. VENABLE.

Received September 9, 1895.

IN a report upon the examination of the chlorides of zirconium<sup>2</sup> it was stated that pure zirconium tetrachloride was formed by the solution of zirconium hydroxide in hydrochloric acid and repeated crystallization from the concentrated acid. This statement was based on a partial analysis by Linnemann<sup>3</sup> the result of which made him call the substance the tetrachloride; and on repeated partial analyses of my own in which the zirconium present was determined by ignition as zirconium dioxide. So firmly convinced was I of the fact that this was the normal tetrachloride that I determined to use it in revising the atomic weight. Ten closely agreeing determinations were made and they yielded as the percentage of zirconium dioxide found 52.99, or, calculating with 90.62 as atomic weight of zirconium (Bailey) 39.16 per cent. of zirconium. The zirconium in the tetrachloride amounts to 38.99 per cent.

Bailey made several very widely differing determinations of the chlorine in this body and considered it the oxychloride. His determinations varied so greatly and his mode of drying were so faulty that I simply concluded he was mistaken, being

<sup>1</sup> Read at the Springfield meeting.

<sup>2</sup> *J. Am. Chem. Soc.*, 1894, 16, 460-475.

<sup>3</sup> *Lond. Chem. News*, 52, 233-240.



unable to detect a source of error in my analyses which would allow for a change from 39.16 per cent. of zirconium to 46.79 per cent., the amount needed for the oxychloride.

Still, as a necessary precaution, I made some determinations of the chlorine in the pure crystalline product and was greatly surprised to find only 35.5 per cent. of chlorine instead of 61.01, the amount required for the tetrachloride. The percentage in the oxychloride would be 36.63.

I regard the results as very singular. The substance must be an oxychloride, but what is its composition? The simplicity of its preparation and the constancy of its composition along with its stability would argue for a simple formula. No such formula can be calculated from the analysis. Probably the best formula suggested for this oxychloride, corresponding closely with the above analysis, is  $\text{Zr}_2(\text{OH})_2\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ .

UNIVERSITY OF NORTH CAROLINA,  
August, 1895.

---

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE ROSE POLYTECHNIC INSTITUTE. No. 7.]

### THE DETERMINATION OF THE HEATING EFFECTS OF COALS.<sup>1</sup>

BY W. A. NOYES, J. R. McTAGGART, and H. W. CRAVER.<sup>2</sup>

Received September 9, 1895.

MANY determinations have been made for the purpose of comparing the heating effect of coals as determined by the calorimeter with that calculated from analyses. Scheurer-Kestner, who seems to have been the first to show that the results obtained in the two ways do not agree, publishes results obtained with the calorimeter of Favre and Silbermann, which differ, in some cases, by ten per cent. from those calculated by Dulong's formula and are uniformly higher.<sup>3</sup> In a later paper<sup>4</sup> he states that he finds lower results with Bertholet's bomb but still results that differ from those calculated.

<sup>1</sup> Read at the Springfield meeting.

<sup>2</sup> The work of which this paper gives an account formed the basis of theses presented to the faculty of the Rose Polytechnic Institute for the degree of Bachelor of Science.

<sup>3</sup> *Compt. rend.*, 106, 1092, 1160, 1230.

<sup>4</sup> *Ibid.*, 112, 233.

Ferd. Fischer claims repeatedly in the *Zeitschrift für angewandte Chemie* and elsewhere that the calorimeter results differ from the calculated heating effect, but admits that the latter may answer for most technical purposes.

Hempel<sup>1</sup> states that the results calculated from careful analyses do not differ more than one or two per cent. from those of the calorimeter and considers that larger differences sometimes found have been due to careless work. He gives six cases of fair agreement, but one which shows a difference of six per cent.

Alexejew<sup>2</sup> gives one case in which the calorimeter result is three and eight-tenths per cent. higher than that calculated.

Scheurer-Kestner<sup>3</sup> has compared the results obtained with Thompson's calorimeter (burning with potassium nitrate and potassium chlorate) with those given by the calorimeter of Favre and Silbermann and finds a maximum difference of three and a half per cent. In using Thompson's method, however, he applies a constant plus correction of fifteen per cent., which F. Fischer criticises as very unreliable.

W. Thompson<sup>4</sup> describes a simple calorimeter which he has devised and gives results obtained with twelve samples of coal. In seven cases the results are lower, in two cases they are the same, and in three cases they are higher than those calculated. F. Fischer<sup>5</sup> criticises these results, saying that the coals were probably not completely burned.

Barrus has described<sup>6</sup> a calorimeter which he appears to have copied from that of W. Thompson.

C. v. John and H. B. Fuller<sup>7</sup> have made a series of comparisons of Berthier's test (reduction of litharge) with the results calculated from analyses. The latter give, in some cases, 900 calories more than the former.

So far as we are aware, no comparisons of this kind have been made with American coals. The work here described was un-

<sup>1</sup> *Ztschr. angew. Chem.*, 1892, 393.

<sup>2</sup> *Ber. d. Chem. Ges.*, 19, 1557.

<sup>3</sup> *Compt. rend.*, 106, 941.

<sup>4</sup> *J. Soc. Chem. Ind.*, 5, 581, and 8, 525.

<sup>5</sup> *Jahrb. chem. Tech.*, 1889, 9.

<sup>6</sup> *Trans. Mech. Eng.*, 14, 816.

<sup>7</sup> *Ztschr. angew. Chem.*, 1893, 285.

dertaken for the purpose of comparing the results obtained with Hempel's calorimeter with those calculated from analyses and those obtained by Berthier's test. Six specimens of representative Indiana coals were used, as follows: Brazil Block from Brazil, Lancaster Block from Clay Co., Shelburn coal from Shelburn, two samples from the mines of the New Pittsburg Coal Co. at Alum Cave, and a sample of mine screenings used in the shops of the Rose Polytechnic Institute. The first two are known locally as "block" coals and are non-coking. The others are known as bituminous and are coking coals.

#### ANALYSES.

The analyses were made as follows:

1. *Moisture*.—One gram of the coal was dried in a toluene-bath (about 105°) for one hour.

2. *Ash*.—The residue of (1) was ignited over a Bunsen burner, at first with a very low flame, till the carbon was completely burned.

3. *Fixed Carbon*.—One gram of fresh coal was placed in a covered platinum crucible and heated with the full flame of a Bunsen burner for just seven minutes. The residue less the ash is the "fixed carbon."

4. *Volatile Combustible Matter*.—The loss of weight in (3) less the moisture is volatile combustible matter.

The above determinations are, of course, of no value for the calculation of the heating effect but give some indication of the character of the coal.

5. *Carbon and Hydrogen*.—About two-tenths gram of the coal was burned in a current of oxygen in a hard glass tube containing copper oxide and lead chromate.

6. *Nitrogen*.—This was determined with soda-lime.

7. *Sulphur*.—Determinations were made by Eschka's method, using potassium carbonate and magnesium oxide, by the method of Carius and by the use of sodium peroxide, as follows: one-half gram of the coal was weighed out in a platinum dish holding about fifty cc. and three grams of sodium peroxide and a little water were added. The whole was evaporated to dryness and ignited. After adding two grams of sodium peroxide and more water the evaporation and ignition were repeated. The mass was then

boiled with water, the solution filtered, acidified, and precipitated as usual. The barium sulphate was purified by fusion with sodium carbonate. The results obtained by this method agreed fairly well with those obtained by Eschka's method, but the results of Carius' method were mostly higher. As a comparison of methods was not part of our plan, the average of the results obtained by Eschka's method are given in the table.

8. *Oxygen*.—In most coal analyses the oxygen has been calculated by subtracting the other constituents, including the ash, from 100. Where the sulphur is low this introduces but a slight error. But with sulphur so high as in some of these coals the error is quite appreciable. The sulphur is mostly present in the form of pyrites and it has been assumed that this is burned to sulphur dioxide and ferric oxide. Accordingly, for the calculation of the oxygen, a correction has been applied to the ash by adding to it five-eighths of the weight of the sulphur present.

The quantities given in the following table are in every case, the average of at least two results obtained by different persons. Where the agreement was not fairly close, a larger number of determinations has been made, and results differing too far from the mean have been rejected. For the results finally used, the average variation from the mean is 0.08 per cent. for carbon, and 0.18 per cent. for hydrogen. These differences correspond to a difference of fifty-seven calories, or about nine-tenths per cent. of the calculated heating effect.

The heating effect is calculated for the coal burned to vapor of water by the formula  $8080C + 28800(H - \frac{1}{8}O) + 1582Fe + 2162S$ , where C, Fe, etc., are the amounts of each element present. As will be seen from the table, the heating effect of the iron and sulphur is quite important in some of these coals.

#### CALORIMETRIC DETERMINATIONS.

The calorimeter used was that described by Hempel.<sup>1</sup> The powdered coal was compressed into cylinders, through which a fine iron wire passed. This wire was weighed, and it was assumed that it gave one-fifth as much heat by its combustion, as the same weight of coal. The autoclave was filled with oxy-

<sup>1</sup> *Ztschr. angew. Chem.*, 1892, 393. See also Hempel's Gas Analysis, translated by L. M. Dennis.

gen, by generating the gas from a mixture of potassium chlorate and manganese dioxide. The temperatures were read by means of a telescope, the thermometer being graduated into fifths. The highest point reached by the thermometer, was used for the calculation. As the rise in temperature was only about five degrees, and the same method was used in determining the water equivalent of the calorimeter, the error due to radiation must have been small. The water used was delivered from a measuring flask, and was found by direct weight to be 997.8 grams. The water equivalent of the autoclave and calorimeter was determined by burning pure sugar charcoal as directed by Hempel. Six determinations gave an average value for the whole, including the water used of 1337.5 grams, with a probable error of five and nine-tenths grams or 0.45 per cent.

At least three determinations were made with each coal. The average difference of the values obtained from the mean for a given coal, was thirty-two calories, or one-half per cent.

The water formed by the combustion in the calorimeter condenses, of course, to liquid water, and, assuming that the average temperature of the calorimeter is  $26^{\circ}$ , a correction of 610 calories per gram of water formed must be subtracted to find the heating effect when burned to vapor of water. The results given in the table have been corrected in this manner.

#### BERTHIER'S TEST.

This was made as follows: One gram of the coal was intimately mixed with forty grams of litharge and the mixture put in a Battersea C crucible, seven and a half cm. deep, and four and a half cm. internal diameter, and covered with a layer of salt. The covered crucible was then placed in a *hot* gas furnace and heated for fifteen or twenty minutes. The crucible was then taken out, tapped to collect the lead, cooled, broken, and the lead button cleaned and weighed.

Theoretically, one gram of lead should correspond to a heating effect in the coal of 234 calories. The results calculated with this factor are, however, about twelve per cent. too low. The average of the results obtained, give an empirical factor of 268.3 calories per gram of lead. The results given in the table have been calculated with this empirical factor.

At least three fairly concordant determinations were obtained for each coal. A few results differing from this mean by more than one-half a gram of lead were rejected. The average difference of the results from the mean for a given coal, was 0.11 gram, which corresponds to twenty-nine calories or about 0.45 per cent.

The following table gives the results of the analyses and other determinations. The differences between the other determinations and those made with the calorimeter are given in per cents.

	New Pittsburg A.	New Pittsburg B.	Lancaster.	Brazil.	Shelburn.	Shop.
Moisture .....	6.83	5.89	12.66	8.98	8.63	2.36
Volatile combustible matter..	39.92	42.23	37.44	34.49	38.82	31.11
Fixed carbon .....	39.93	40.40	47.22	50.30	43.45	42.44
Ash .....	13.31	11.48	2.68	6.23	9.05	24.09
Carbon .....	62.88	65.26	71.41	70.50	66.86	57.32
Hydrogen .....	5.07	5.17	5.56	4.76	5.30	4.56
Nitrogen .....	1.01	1.17	1.54	1.36	1.50	1.44
Oxygen .....	13.06	13.25	18.42	16.29	15.69	9.93
Ash (corrected).....	17.98	15.15	3.07	7.09	10.65	26.75
Sulphur .....	7.46	5.88	0.62	1.39	2.57	4.25
Iron, calculated .....	6.53	5.14	0.54	1.22	2.25	3.72
Calories per gram, calc'd C	5081.	5272.	5770.	5696.	5402.	4632.
“ “ “ “ H	991.	1011.	939.	784.	962.	956.
“ “ “ “ S	161.	127.	13.	30.	55.	92.
“ “ “ “ Fe	103.	81.	9.	19.	36.	59.
Total	6336.	6491.	6731.	6529.	6455.	5739.
Difference, per cent.....	+2.6	+1.2	+0.4	-4.6	-1.2	-1.2
Calories per gram, Berthier's test, factor 268.3.....	6307.	6471.	6831.	6689.	6461.	5726.
Difference, per cent.....	+2.1	+0.9	+1.9	-2.3	-1.1	-1.4
Calories per gram, calorimeter	6175.	6415.	6703.	6846.	6532.	5806.

In discussing the results, it is worth while to notice that, so far as indicated by the agreement of duplicate determinations, about the same degree of uncertainty attaches to the calorimetric determinations and to the litharge test, while the uncertainty of the analysis is about twice as great. It is noticeable that the results calculated from the analyses, and those given by

Berthier's test, agree better with each other than either agree with the calorimeter results.

On the average Berthier's test, when the empirical factor is used, appears to be more reliable than the results calculated from the analyses.

While the differences between the results obtained by different methods are not very great, they are certainly greater than can be accounted for by the errors of the work. In the case of two of the most important coals, the Lancaster and Brazil black, the relative value of the coals as given by the calorimeter, is reversed as given by the analyses and by Berthier's test. There can be little doubt that the calorimeter gives most accurately the relative heating value of these coals.

Attempts to make determinations with anthracite coals were unsuccessful, because it was found impossible to compress it into cylinders, and we have not yet been able to burn it in the form of a powder.

Some attempts have also been made to use the calorimeter of Barrus,<sup>1</sup> but a deposit of carbon was always formed, and the results appeared to be entirely unreliable. It is probable that the results would be more satisfactory with anthracite coals.

TERRE HAUTE,  
INDIANA.

---

## TELLURIUM: ITS SEPARATION FROM COPPER RESIDUES WITH NOTES ON SOME NEW REACTIONS.<sup>2</sup>

BY CABELL WHITEHEAD.

Received Sept. 9, 1895.

**T**ELLURIUM which a few years ago was classed as a rare metal, is now known to be distributed over a very wide area, not only in our western states, but also in the gold producing states of the east. It occurs in the free state, and also combined with gold, silver, bismuth and many other metals. In the state of Colorado, tellurium is found in combination with gold and silver to such an extent, that the ores in many districts are rendered unfit for amalgamation, and smelting and chlorination has to be resorted to. The separation of silver and gold from low grade

<sup>1</sup> Trans. Mech. Eng., 14, 816. See also W. Thompson, *loc. cit.*

<sup>2</sup> Read at the Springfield meeting

telluride ores, is a problem which, up to the present time, has baffled the skill of the metallurgists of the world. A few of the difficulties may be mentioned as follows: Tellurides do not give up their gold to mercury, cyanide or chlorine, they concentrate badly, a large percentage of the value being lost as slimes. They are difficult to roast, on account of their low melting-point and the loss of gold, during the removal of the tellurium. The usual course is to smelt this class of ore either with lead or copper ores. It is to the latter method I will call especial attention in this paper.

In order to work the copper ores of the west economically, they are smelted with gold and silver-bearing ores which act as flux, and also enrich the matte produced to a point where the cost of refining the copper is more than covered by the value of the precious metals contained. In this way large amounts of tellurium enter the matte. These mattes are Bessemerized in the west, and copper brought east to be refined by electrolysis. It contains from 98.5 to 99.5 per cent. copper, about 100 ounces of silver, and three-tenths ounce of gold per ton. The impurities are arsenic, antimony, lead, bismuth, tellurium and selenium. The average amount of tellurium is not far from 0.04 per cent. or 0.8 of a pound per ton. With the possible exception of the native copper of Lake Superior, it is doubtful if any copper produced is free from tellurium; this is certainly true of that from sulphide ores. I have already described a method for estimating the tellurium under these circumstances.<sup>1</sup>

The electric refining of such copper is carried on at Anaconda and at the Boston and Montana Copper Co. works at Great Falls, Montana; the Baltimore Electric Refining Co., Baltimore, Maryland; the Bridgeport Copper Co., Bridgeport, Conn., and the Ansonia Refining Co., Ansonia, Connecticut; the Central Falls Electric Refining Co., Central Falls, Rhode Island; the Washburn and Moen Co., Worcester, Mass. and perhaps others.

In the Hayden process a bath of dilute copper sulphate, acidified with sulphuric acid is employed, in which is inserted an anode of rolled black copper and a cathode from a strip of pure copper, each being connected with the electric generator, while

<sup>1</sup>*J. Am. Chem. Soc.*, 17, 280, 1895.



disconnected plates of black copper are suspended in the bath between the two electrodes. When the current is on, solution takes place, not only at the anode but on all the disconnected plates interposed between the electrodes, and what is more interesting, this solution takes place on those surfaces of these plates which face the negative electrode, while the deposition of the pure copper takes place on the surface of the adjacent plate which faces the positive electrode. When the copper goes into the solution in its bath small amounts of some of the impurities in the copper enter into solution with it, but the greater portion remains either in the metallic state or are converted into oxides or basic salts which fall to the bottom of the bath where they form a black slimy residue.

The commercial refining of these residues is carried out as follows:

After screening out the coarser copper, the slimes are boiled with a twenty per cent. solution of sulphuric acid in a lead-lined tank by live steam, air being drawn in with the steam by means of a peculiar injector. During this boiling, practically all of the antimony, arsenic and bismuth salts, together with copper in the oxidized condition and that small portion of metallic copper which has been oxidized by the injected air go into solution.

After about one hour's boiling, a solution of silver sulphate is run in and steam applied for some minutes whereby according to the reaction  $\text{Cu} + \text{Ag}_2\text{SO}_4 = \text{CuSO}_4 + \text{Ag}_2$ , the metallic copper still remaining is rapidly and completely converted into copper sulphate. Any excess of silver sulphate is removed by the addition of a fresh portion of slimes, when the solution is drawn off and the residue washed until free from copper salts. This residue, which has now lost the slimy, adhesive properties which characterized it and which consists of gold, silver, tellurium, and lead sulphate is pressed on a filter press. The pressed cakes are dried in an oven and then melted in a furnace, having a bed made of Portland cement, which is so arranged that a blast may be turned on. This quickly removes all but a trace of the lead present, together with portions of the tellurium and selenium.

The resulting bullion is poured into shoe-bars, weighing about 300 ounces each, it is about 950 fine, in silver and ten parts of

gold. When cool these bars are dissolved in hot sulphuric acid, in a cast iron kettle, and when solution is complete the liquid is allowed to cool and settle for several hours, during which the gold falls to the bottom and the tellurium crystallizes out in white lustrous crystals of tellurous oxide. The first portion of the clear liquid is drawn off and precipitated by metallic copper, and the silver melted into bars 990 fine. The remainder is used in treating a fresh portion of the slimes.

The gold and the tellurous oxide are allowed to accumulate in the kettle until several hundred ounces are at hand, when they are removed and washed with dilute sulphuric acid and water, to remove silver, copper sulphate and tellurous oxide, and afterwards boiled in a small kettle with concentrated sulphuric acid to remove the remaining portion of silver and tellurium. When cool, and the gold has settled, the acid is again drawn off and the residue washed until free from tellurium and silver sulphates. The gold is now melted with borax and niter, by which any remaining traces of lead and tellurium are oxidized and slagged off, leaving fine gold, over 990 fine, the impurity being silver.

The washings from the gold residue contain the tellurium as tellurous oxide or tellurous sulphate. The tellurium may be obtained from these in two ways, after the removal of the silver as chloride. First, by precipitation with copper; second, by passing sulphur dioxide through the solution. It is better to use the first method, as large quantities of sulphur dioxide are very disagreeable to handle, and as the tellurium thus precipitated in the presence of copper is not pure and requires a further treatment. The metal used in this work was produced by inserting bars of copper into the solution and boiling with steam, a precipitate of cuprous telluride being obtained as a black powder. This was dried and then boiled with a five per cent. solution of sulphuric acid to remove the copper which had been oxidized during the drying process. After filtering, the mass is again moistened with five per cent. sulphuric acid and subjected to atmospheric oxidation with frequent stirring, then boiled again with more sulphuric acid and washed, this process is repeated until the copper is eventually very completely removed. Any copper left will combine with tellurium when fused and

cause loss. The residue is now dried, mixed with three times its weight of sodium carbonate, and one-fourth its weight of charcoal, melted in a French clay crucible to quiet fusion, brought almost to a white heat, and the melt poured into a suitable mold. The cooled mass is crushed to a powder and the sodium telluride formed, dissolved out with boiled water; a great amount of heat is developed during the solution. The solution thus produced, which possesses a rich port wine color, is filtered off, and the tellurium precipitated in the metallic state, by the passage of a current of air, as a fine gray powder, looking not unlike finely powdered galena. The tellurium is filtered and boiled with dilute hydrochloric acid, to remove traces of iron, alumina, etc., washed and boiled for several hours, with a concentrated solution of potassium cyanide which removes selenium and most of the gold present. After drying, the tellurium is melted, without flux, in a French clay pot, the fine particles are made to run together by stirring, only a low temperature is necessary and the loss by volatilization is small. The metal still contains traces of impurities, the chief of which is gold. This would indicate that sodium telluride is a solvent of metallic gold, but this has not yet been proven. The tellurium is further purified by distillation in hydrogen gas.

#### NEW REACTIONS OF THE SALTS OF TELLURIUM.

If to a solution of the sodium or potassium tellurite is added a solution of an ammonium salt, such as the chloride or nitrate, a white precipitate is thrown down, which on boiling becomes granular.



A small amount of tellurium dioxide or a metal which can be precipitated by sulphur dioxide remains in solution. It is the intention of the writer as soon as possible to examine and compare the properties of the metal from this fractional precipitation. While it is probable that tellurium oxide is slightly soluble in the alkali salts formed, which would explain incomplete precipitation, in view of the growing belief in the compound nature of tellurium, this reaction is deemed worthy of further investigation.

In an effort to purify tellurium, based upon the well-known property of hydrogen telluride of precipitating many of the

# 854 TELLURIUM: ITS SEPARATION FROM COPPER RESIDUES.

metals from solution, the following reaction was observed, in addition to the one expected:  $\text{TeCl}_4 + 2\text{H}_2\text{Te} = 3\text{Te} + 4\text{HCl}$ . By passing this gas for some time into a solution of tellurium chloride, made slightly acid with hydrochloric acid, there was obtained a precipitate of tellurium and tellurides and a solution, from which sulphur dioxide threw down a precipitate of tellurium. After distillation in hydrogen I propose to determine the atomic weight of this purified metal.

When potassium ferrocyanide is added to tellurium chloride no change is observed at first but after a few hours Prussian blue is formed in large quantities.

## ALUMINUM TELLURIDE.

Tellurium when heated with aluminum combines with explosive violence, forming a chocolate colored, difficultly fusible compound having the following composition by analysis.

	Per cent.
Aluminum .....	12.78
Tellurium .....	87.22
	<hr/>
	100.00

This corresponds closely to the formula  $\text{Al}_3\text{Te}_2$ , which requires

	Per cent.
Aluminum .....	12.58
Tellurium .....	87.42
	<hr/>
	100.00

The violent chemical action attending its formation, joined with the fact that its composition remains constant, even in the presence of a large excess of aluminum, would indicate a true chemical combination and not an alloy, in the accepted sense. It is hard and brittle, can be easily ground to powder. When exposed to moist air it is slowly decomposed with the liberation of hydrogen telluride. When thrown into water hydrogen telluride is rapidly given off according to the following reaction:  $\text{Al}_3\text{Te}_2 + 3\text{H}_2\text{O} = \text{Al}_3\text{O}_2 + 3\text{H}_2\text{Te}$  which corresponds to the well known sulphur reaction  $\text{Al}_3\text{S}_2 + 3\text{H}_2\text{O} = \text{Al}_3\text{O}_2 + 3\text{H}_2\text{S}$ . While comparing these two reactions it may be noted that hydrogen telluride is much more easily decomposed by oxygen than hydrogen sulphide. For example in treating aluminum telluride with

water which has not been boiled fully one-half of the tellurium remains as metal:  $\text{H}_2\text{Te} + \text{O} = \text{H}_2\text{O} + \text{Te}$ . When treated with ninety-five per cent. alcohol no reaction takes place, even on boiling. This would seem to be the best one of the tellurides from which to make the organic salts as it does not decompose in the air so quickly as the alkali tellurides.

SEPARATION FROM COPPER BY THE ELECTRIC CURRENT.

Tellurium is easily deposited by the current, either from acid or alkaline solutions; even the feeblest current throws out the metal, but unfortunately not in the reguline state.

It has been found possible to separate tellurium from copper by adding an excess of sodium hydroxide and about three grams of potassium cyanide for each gram of copper present. With this solution, a current such as is used for depositing copper, will throw out all the tellurium present, as a black non-adherent precipitate. After twelve hours, the tellurium is filtered off and weighed, either as metallic tellurium on a weighed filter or as tellurium dioxide. The solution is now made slightly acid with sulphuric and the copper precipitated in the usual way. If the proper amount of potassium cyanide has been added and the current has not been allowed to run too long, the tellurium is perfectly free from copper, and if the current is strong enough, none of it will adhere to the cathode.

COLUMBIAN UNIVERSITY, WASHINGTON, D. C.

## THE ELECTROLYTIC REDUCTION OF PARANITRO COMPOUNDS IN SULPHURIC ACID SOLUTION.<sup>1</sup>

BY ARTHUR A. NOYES AND JOHN T. DORRANCE.

Received September 9, 1895.

### INTRODUCTION.

IT was shown some time ago by Noyes and Clement<sup>2</sup> that nitrobenzene in sulphuric acid solution is transformed by electrolytic hydrogen into paraamidophenolsulphonic acid. It has since been proved by the extended investigations of Gattermann and his students<sup>3</sup> that this behavior is characteristic of aromatic nitro compounds in general, one of the oxygen atoms

<sup>1</sup> Read at the Springfield meeting.

<sup>2</sup> *Ber. d. chem. Ges.*, 26, 990.

<sup>3</sup> *Ibid.*, 26, 1844, 2810; 27, 1927.

of the nitro group always migrating during the reduction to the para position with the production of a hydroxyl group. It is evident, however, that this cannot take place when the position para to the nitro group is occupied by another element or group than hydrogen. The purpose of our investigation was to determine the nature of the reduction-products of a number of such compounds with the view of ascertaining any general principle that may exist. Only three such para compounds have been previously studied, namely, paranitrotoluene and paranitroorthotoluidine by Gattermann<sup>1</sup> and paranitrobenzoic acid by Noyes and Clement.<sup>2</sup> We have now investigated three additional ones, paranitraniline, paranitrophenol, and parachloronitrobenzene.

#### THE METHOD OF REDUCTION.

The method of carrying out the reduction was essentially the same in all cases. The apparatus consisted of a small beaker, to the sides of which a large platinum electrode was closely fitted, and in which was placed a cylindrical porous cup containing a small platinum electrode. Concentrated sulphuric acid was placed within the cup at the start, and small quantities of diluted acid were occasionally added during the electrolysis to prevent the acid from becoming fuming. The solution to be electrolyzed was placed outside; it was prepared by dissolving twenty or thirty grams of the substance in two and a half to three times its weight of strong sulphuric acid. A current of one or two amperes was passed through for forty or fifty hours.

The reduction-product precipitated either during the electrolysis or after cooling. It was filtered out upon a hardened filter with the aid of suction and dried by spreading on porous plates. The filtrate was diluted with an equal bulk of water, and any further precipitate added to the original one. The subsequent purification varied in the different cases, and will be described under the separate substances.

#### REDUCTION OF PARANITRANILINE.

The paranitraniline used was in part a Kahlbaum preparation and was in part prepared by ourselves by the method given by

<sup>1</sup> *Ibid.* 26, 1850, 1852.

<sup>2</sup> *Am. Chem. J.*, 16, 511.

Nölting and Collin.<sup>1</sup> It gave the correct melting-point of 146°.

The reduction-product was isolated by extracting the precipitate dried on the porous plates with boiling water, boiling the solution with animal charcoal, filtering, and causing to crystallize by cooling.

It was found to consist of paradiamidobenzene sulphate. It was very difficultly soluble in cold water.<sup>2</sup> Its solution was colored purple by ferric chloride, and it gave the following results on analysis:

0.2193, 0.2847, and 0.3581 gram substance gave respectively 0.0985, 0.1262, and 0.1638 gram water and 0.2822, 0.3672, and 0.4605 gram carbon dioxide.

0.3147, 0.2077, 0.3938, and 0.4525 gram substance gave respectively 0.3481, 0.2340, 0.4363, and 0.5066 gram barium sulphate.

	I.	Found. II.	III.	IV.	Calculated for $C_6H_4N_2SO_4$ .
Carbon.....	35.10	35.18	35.08	....	34.94
Hydrogen.....	4.99	4.92	5.08	....	4.85
Sulphur trioxide	38.32	38.68	38.04	38.44	38.84

#### REDUCTION OF PARANITROPHENOL.

A sample of the substance from Kahlbaum having the correct melting-point (113°) was employed.

The reduction-product was practically insoluble even in boiling water, but dissolved readily in sodium hydroxide or carbonate. It was purified by dissolving in the latter, filtering, and precipitating immediately with hydrochloric acid. The precipitate was washed successively with water, alcohol, and ether, and dried at 125°. Twelve grams were obtained from thirty grams of nitrophenol.

The physical and chemical properties and the analysis of the body established its identity as paraamidophenolsulphonic acid. It reduced silver nitrate solution in the cold with the production of a purple color, and turned brown rapidly in alkaline solution owing to oxidation. It was decomposed by heating with strong

<sup>1</sup> *Ber. d. chem. Ges.*, 17, 262.

<sup>2</sup> Contradictory statements exist in the literature as to the solubility of this salt. Nietski, in *Ber. d. chem. Ges.*, 11, 1098, states that it is readily soluble. Vignon, in *Bull. Soc. Chim.*, 50, 153, that it requires 714 parts of water at 15°. The latter statement is, according to our experience, the correct one.

hydrochloric acid in a closed tube to  $180^{\circ}$ ; the hydrochlorate of the base crystallized out upon cooling, and from this, by the addition of potash, the base itself was set free. Like paraamidophenol, it melted at  $183^{\circ}$ , undergoing decomposition. It also showed the characteristic color reactions of that substance with chloride of lime and ferric chloride.

The analysis of the sulphonic acid gave the following results:

0.2361 gram substance gave 0.0879 gram water and 0.3295 gram carbon dioxide.

	Found.	Calculated for $C_6H_5.NH_2.OH.SO_3H.$
Carbon .....	38.06	38.08
Hydrogen .....	4.13	3.70

#### REDUCTION OF PARACHLORNITROBENZENE.

A Kahlbaum preparation (melting-point  $83^{\circ}$ ) was employed in this case also. The reduction-product proved to be a sulphonic acid, and was purified exactly as that obtained from the reduction of nitrophenol. It was first tested qualitatively for chlorine and found to contain none. It exhibited in fact all the characteristic properties of paraamidophenolsulphonic acid, being almost insoluble in hot water, oxidizing very rapidly in alkaline solution, and readily reducing silver nitrate solution. It was subjected to just the same treatment as the reduction-product of the nitrophenol with identical results. In addition to the confirmatory tests described under that substance, the diacetyl derivative of the base was prepared by boiling with acetic anhydride, and this was found to melt at  $149^{\circ}$ . Diacetyl-paraamidophenol melts according to Ladenburg at  $150^{\circ}$ – $151^{\circ}$  C.

The sulphonic acid gave the following results on analysis:

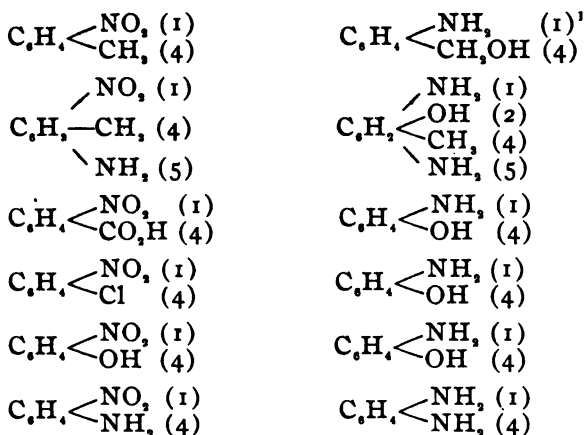
0.2912 gram substance gave 0.1002 gram water and 0.4059 gram carbon dioxide.

	Found.	Calculated for $C_6H_5.NH_2.OH.SO_3H.$
Carbon .....	38.02	38.09
Hydrogen .....	3.90	3.70

#### SUMMARY OF THE RESULTS.

The paranitro compounds, which up to the present time have been submitted to electrolytic reduction are tabulated below together with their reduction-products:





The most striking of the results are those obtained with the paranitrobenzoic acid and with the parachlornitrobenzene, the group para to the nitro group being driven out in each case. It seems not improbable that this behavior is a general characteristic of nitro compounds with negative para groups, but an investigation of others would be needed in order to establish it as a fact.

It is also worthy of note that, contrary to what might be expected, in only one of the six cases, that of the nitrotoluidine, does the oxygen atom display any tendency to migrate to any other than the para position.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,  
BOSTON, MASS.

## PERIODIDES OF PYRIDINE.<sup>2</sup>

BY A. B. PRESCOTT AND P. F. TROWBRIDGE.

Received September 20, 1895.

### PYRIDINE ALKYL PERIODIDES.

I. *Pyridine Methyl Pentiodide*.—This was obtained in the manner given in detail below, very satisfactorily in preparation I, and with slight impurity in two other preparations, II and III, by different ways, through separation from other periodides.

<sup>1</sup> The substance isolated was a condensation-product of this with a second molecule of nitrotoluene; but this is undoubtedly the primary reduction-product.

<sup>2</sup> Read at the Springfield meeting of the American Association for the Advancement of Science, September 2, 1895.

Preparation I is in greenish-black long needles of very dark green luster, some of the crystals being nearly two inches in length. The melting-point is  $47.5^{\circ}\text{C}.$ <sup>1</sup>

Preparation II is of small quantity, in greenish-black crystals, very hard and compact, melting at  $47^{\circ}\text{C}.$

Preparation III is in crystals exactly like I, melting at  $47^{\circ}\text{C}.$ , by recrystallization in alcohol from a greenish-black crystalline powder, the latter being stable and melting at  $43^{\circ}\text{C}.$  The analysis of III was obtained only from this powder, before the final crystallization. These three preparations are, alike, so far stable that after keeping eight months in glass-stoppered bottles, most of the time in the dark, the glass is but just perceptibly stained with iodine liberated from decomposition.

The analyses of the methyl pentiodide, by methods detailed further on, gave results as follows:

	Calculated for $\text{C}_5\text{H}_5\text{N}.\text{CH}_2\text{I}_4.$	I.	Found. II.	III.
Iodine total .....	87.06	86.74	....	86.69
Iodine by titration....	69.65	68.87	69.83	69.55

2. *Pyridine Methyl Diiodide*.—Obtained through different ways, as stated later, in two preparations. I is in reddish-brown crystals, thick plates, compact in clusters. Some crystals are an inch long and a fourth of an inch wide. Melting-point,  $91.5^{\circ}\text{C}.$  The crystals are very stable. On eight months' standing there are no perceptible results of decomposition. II is in red interlaced fine needles of good length, the last previous crystallization having been in dark-red sheaf-form clusters of great beauty. Melting-point,  $91.0^{\circ}\text{C}.$  In stability II is equal to I.

The analyses, with duplicates as specified later, gave the following:

	Calculated for $\text{C}_5\text{H}_5\text{N}.\text{CH}_2\text{I}_2.$	I.	Found. II.
Iodine total .....	72.91	72.88	72.33
Iodine by titration .....	36.55	36.97	36.40

3. *Pyridine Methyl Triiodide*.—Obtained in three preparations, each from a separate recrystallization out of a common mother-

<sup>1</sup> Measurements of the crystals, and various optical determinations, as well as work by other physical methods, especially such as bear upon molecular weight and constitution, are reserved together for a continued investigation of these bodies.

liquor, that of II of the methyl diiodide. Again it is obtained in the first crystallization by another method, that for IV. I is in dark-red fine needles, quite perfect in outline and partly clustered in certain sheaves characteristic of the earlier crystallizations of this triiodide. Melting-point,  $50^{\circ}$  C. Perfectly stable.

II shows dark-red needles, the previous crystallization having been merely a loose crystalline mass. Obtained perfectly stable, with melting-point of  $50^{\circ}$  C.

III is dark-red needle clusters of a certain exact sheaf-form appearing illusively in several earlier crystallizations. But a small quantity was obtained, with a melting-point of  $49^{\circ}$ – $50^{\circ}$  C.

IV, perhaps the most perfect, is in very dark red or reddish-black plates with needles, perfectly stable, and melting at  $48^{\circ}$  C.

The results in analysis have been these :

	Calculated for $C_6H_5N.CH_2I.I_2$ .	I.	Found. II.	III.	IV.
Iodine total.....	80.14	79.32	79.22	....	78.70
Iodine by titration.....	53.43	53.08	51.52	52.75	53.15

4. A product was obtained of seeming distinct character, in composition and melting-point nearly approaching the pentiodide, but with the elemental figures of a tetrapentaiodide, that is, dipyridinedimethylenneaiodide. It is reserved for further work. It is in greenish-black, lustrous, long needles, well defined, of a melting-point of  $44^{\circ}$  C. The total iodine in three successive determinations was found to be, respectively, 85.83, 85.88, and 85.83 per cent. ; calculation for  $(C_6H_5N.CH_2I)_4I_4$ , giving 85.68 per cent., and for  $C_6H_5N.CH_2I.I_2$ , 87.06 per cent. The iodine by titration was found to be 67.52, 67.08, 67.02, and 66.69 ; calculation giving for these formulas, respectively, 66.45 and 69.65 per cent.

5. *Pyridine Methyl. Octaiodide*.—This product is named provisionally, one fairly satisfactory preparation of it being obtained, a second preparation having the requisite composition but (possibly from its more compact crystallization) having a higher melting-point, and a third preparation, while agreeing in melting-point with the first, falling too low in percentages of iodine. The preparation, detailed below, was instituted in the hope of obtaining the enneaiodide. I, by recrystallization from alcohol below

0° C., is greenish-black, in both plates and needles, melts at about 26° C., and is fairly stable when kept at about 15° C. or below. II is in crystals of the same color as those of I, but more slowly formed and more compact, consisting of flat needles, some of them an inch long, with melting-point of about 41° C.. III was imperfectly crystallized, rather solidified in a crystalline mass, of the color of I, and melting at 25° C. We do not include III among the determinate preparations. It gave of total iodine, 90.36 per cent., and of iodine by titration 78.41 per cent., both figures being low for the octaiodide and much too high for the heptaiodide.

	Calculated for $C_6H_5N.CH_2I.I_7$ .	I.	Found. II.
Total iodine.....	91.51	90.79	90.99
Iodine by titration .....	80.07	79.82	80.13

6. *Pyridine Ethyl Triiodide*.—Obtained, as specified under the account of preparations, from liquid secondary products corresponding to those which gave the three samples of the pyridine methyl triiodide, in lustrous greenish-black needles, well defined, stable through exposure to the air, and melting at 49° C. In the analysis, two determinations by silver iodide gave for iodine 78.389 and 78.388. Three titrations with the thiosulphate gave for iodine 52.784, 52.612 and 52.616. Inasmuch as the mother liquids have been found to contain higher periodides, it is evident that these crystals are not wholly freed from mother liquid.

	Calculated for $C_6H_5N.C_2H_5I.I_3$ .	Found.
Iodine total.....	77.85	78.39
Iodine by titration.....	51.90	52.67

7. Higher ethyl periodides of pyridine, in nearly black crystals melting below 10° C., were indicated from treatment of the primary oil-like product, though not yet obtained in purity, as stated under the preparation of the triiodide.

*Methods of Preparation*.—The methyl periodides of pyridine are best obtained, first, by adding the methyl normal iodide of pyridine to dissolved iodine. We have also obtained several pyridine methyl periodides; second, by adding pyridine to a solution of methyl iodide and iodine. We have found, however, as stated further on, that in the latter way there is formed some proportion of a pyridine periodide destitute of methyl, though

the avidity of pyridine for methyl iodide ensures a considerable proportion of methyl periodides. For pyridine ethyl periodides the second way would not promise formative results at all owing to the tardy addition of ethyl iodide to pyridine. The normal pyridine alkyl iodides used were prepared for the purpose, and had the properties specified in another paper by one of us (P), in which, also, is a statement of the constants of the pyridine used in these preparations. In adding the pyridine alkyl normal iodide to iodine, the latter was taken in the proportion to make the particular periodide desired, but other periodides would appear as subordinate products. As to just how much effect the relative quantity of iodine added exerts upon the extent of iodine combination, further investigation is now in progress.

The preparation of pyridine methyl pentioidide was done as follows: Eighteen grams of pyridine methyl iodide dissolved in a little alcohol were added to fifty grams of iodine previously dissolved in 200 cc. of alcohol, the solutions being taken at low temperature. A dark green oil-like liquid, thick and cohesive, at once separated in abundance at the bottom. The thin alcoholic liquid above was decanted off and the oil set aside at temperature several degrees below  $0^{\circ}\text{C}$ ., when it shortly solidified in crystals, not melting at  $25^{\circ}\text{C}$ . These were dissolved in warm alcohol, and the solution set aside at about  $-5^{\circ}\text{C}$ ., when crystals of preparation I appeared. They were dried over sulphuric acid to a constant weight, for analysis and determination of the melting-point. This periodide was undoubtedly obtained in its amorphous oil-like state by O. Lange in 1885<sup>1</sup> while engaged in obtaining decomposition products of pyridine methyl iodide by Ladenburg's process. He reported obtaining the heavy dark-green oil, which would not solidify on standing for a day, and which he apparently did not analyse.<sup>2</sup> III of the methyl pentioidide was obtained by treating a part of the first crystalline form of the methyl octaioidide before described, with ether, which

<sup>1</sup>On Picolines, *Ber. d. Chem. Ges.* 18, 3436.

<sup>2</sup>It was in following Lange that this preparation I of the methyl pentioidide was first undertaken, and the "oil" obtained. After fruitless attempts to crystallize it from various solvents, it was abandoned for six weeks, when, on one very cold day, in moving things it was set in the window next the glass, and presently it became a mass of crystals. These did not melt when returned to the warmer air of the laboratory. A new preparation was at once commenced as above.

dissolves a small portion of the crystals, leaving the remainder as this preparation III of the pentiodide. Preparation II of the methyl pentiodide was obtained from the mother liquor of the methyl octaiodide by evaporation and redissolving the crystals in alcohol.

The preparations of the pyridine methyl diiodide in I and II were from solutions quite different from each other from the beginning, but in both cases they were from later crops of crystals following the addition of free pyridine to solution of the other two materials. The final crystals of I were washed in a very little cold alcohol, and then dried over sulphuric acid for ten days. The crystals of II were obtained fine by rapid formation in alcohol surrounded by a freezing mixture.

The preparations of pyridine methyl triiodide in I, II and III were crystallized from the mother liquids of II of the corresponding diiodide. II of the triiodide was itself recrystallized several times. I and III were in more compact crystals of slower formation. But IV was the result of a different method throughout, following the addition of iodine solution to the methyl normal iodide, using proportions intended for the diiodide. The final crystals were by a single recrystallization of the first crop. It was dried between filter papers over sulphuric acid.

The preparations of pyridine methyl octaiodide (provisionally so termed) were instituted by adding eleven grams of the normal iodide dissolved in a little alcohol, to fifty-five grams of iodine in as little alcohol as possible, both solutions being hot. The greenish black oil-like mass separated at once. The decanted solution was cooled, and other portions of the oil obtained. Below  $0^{\circ}\text{C}$ . the oil crystallized well. I was crystallized from solution in alcohol at low temperature. II was crystallized from alcohol by spontaneous evaporation out of doors in cool weather. The final crystals of each were dried between filter papers, and kept in the vault at about  $12^{\circ}\text{C}$ .

Pyridine ethyl triiodide was obtained following the addition of alcoholic solution of the normal iodide to alcoholic solution of iodine. The first product, chiefly higher iodides, appeared in an oil-like precipitate, and this, after decanting the alcoholic liquid, was dissolved in hot alcohol, and the solution kept for six

hours at  $-4^{\circ}$  C. without obtaining crystallization. Afterward crystals were obtained but without success in drying them. Moist with the oil they gave figures a little too low for the tetraiodide. Repeating the entire operation, but not decanting the oil, the entire mixture was exposed to low temperature as before, and the oil solidified in a mass of fine crystals better than before, but these melted below  $10^{\circ}$  C., and the attempt to obtain a pure high periodide had to be deferred. That the oil, which is stable when dried and has no odor of iodine, contains high iodine additive combination was shown by its analysis, giving figures midway between hexiodide and heptiodide. Now the alcoholic liquid decanted from the oil in the first operation, on cooling below  $0^{\circ}$  C., gave an excellent crop of crystals. These, dried for several days over sulphuric acid, at about  $21^{\circ}$  C., constitute the preparation described under the name pyridine ethyl triiodide.

PERIODIDES OF THE AMINE AND OF THE TERTIARY  
AMMONIUM BASE.

1. *Pyridine Tetraiodide*,  $C_5H_5N.I_4$ .—Adding to pyridine an alcoholic solution of iodine until the precipitate ceased to form, thereby leaving a slight excess of iodine, there was obtained a bulky crystalline precipitate of a green color, not of a red color as reported by Dafert.<sup>1</sup> This precipitate was filtered out, drained, washed with alcohol, and drained dry, all under the filter pump, then dried between filters over sulphuric acid for several days. It was found soluble in alcohol, ether, chloroform, and less readily in benzene. It was recrystallized from benzene in I, from chloroform in II, and from alcohol in III. In each result the crystals were dark lustrous green. Those of III were in button-like aggregations of fine needles, the whole about half an inch in diameter. From each solution the crystals showed the same melting-point,  $85^{\circ}$  C. The alcoholic mother-liquor on evaporation gave a crop of very small dark-green crystals IV of the same melting-point. All these crystals gave off perceptible traces of iodine on standing in a glass-stoppered bottle, being very perceptibly less stable than the crystal preparations of the various pyridine *quaternary* base periodides already described. This instability may be the cause of the slight deficiency of iodine found in analysis, the resulting figures being as follows:

<sup>1</sup> 1883, *Monatsh. Chem.*, 4, 509.

	Calculated for $C_5H_5N.I_4$	I.	Found.		
			II.	III.	IV.
Iodine total, by silver iodide .....	86.49	85.72	85.94	85.63	85.48
Iodine by titration with thiosulphate		85.05	84.79	85.73	85.63

This periodide, therefore, contains no iodine firmly bound as in all normal iodides, none that is not promptly taken up by thiosulphate. In this constitutional feature it is a periodide sharply unlike all the pyridine alkyl periodides known, and unlike the pyridine hydrogen pentiodide found by Dafert,<sup>1</sup> and further described below as examined by us. A superbromide of pyridine was obtained, in 1882, by Grimaux,<sup>2</sup> who writes for it the formula,  $(C_5H_5NBr_3)HBr$ . He found it not very stable; in analysis he made but one estimation of bromine, that by silver bromide; and he found the compound reduced by hydrogen sulphide to pyridine hydrobromide and hydrobromic acid. The triethylphosphine tetraiodide,  $P(C_2H_5)_3I_4$ , *inferred* by Masson and Kirkland in 1889,<sup>3</sup> is of the same type as our pyridine tetraiodide. Treated with hydrogen sulphide half its iodine entered into phosphonium normal iodide, and half into hydriodic acid.

Several months before the preparation of pyridine tetraiodide as above given, a product was obtained in another way which puzzled us at the time, but which we now recognize as this last-formed pyridine tetraiodide. It was obtained in the first crystalline precipitate after adding free pyridine to the solution of methyl iodide and iodine, in the second way for making the methyl periodides. The mother-liquor of the precipitate gave us the methyl diiodide, preparation I of that product. The precipitate itself crystallized from a chloroform solution, gave very dark green short needles, melting at  $84.5^\circ$  C., and soluble in ether and in benzene. The total iodine was found as 86.32 per cent (the average of four results, lowest 86.22, highest 86.50). At that time a satisfactory titration for iodine was not obtained

<sup>1</sup> F. W. Dafert, 1883, *Monatsh. Chem.*, 4, 508. Dafert says, p. 509, "In alkoholischer und in wässriger Lösung des Pyridins erzeugt Iod in Alkohol, respective in Iodjodkaliumlösung ebenfalls unter gewissen umständen eine Fällung. Eben so bei Anwendung von Schwefelkohlenstoff. Das dabei erhaltene Präparat ist roth gefärbt und jedenfalls mit dem obigen Superiodid *nicht* identisch. Eine weitere Untersuchung wird wohl näheres ergeben." We have not been able to find a further publication by Dafert upon this compound.

<sup>2</sup> E. Grimaux, *Compt. rend.*, 95, 87; *Bull. Soc. Chim.*, 38, 127.

<sup>3</sup> *J. Chem. Soc.*, 55, 139.



on account of the solvent, but without any solvent one slow titration resulted in 85.82 per cent., indicating the absence of normal iodine, when the preparation was put aside for later inquiry. It appears, therefore, that when free pyridine is added to methyl iodide and iodine, in alcoholic solution of each, some periodide of pyridine without methyl is formed in the first precipitate, notwithstanding the extreme avidity with which pyridine unites directly with methyl iodide.

2. *The Pyridine Hydrogen Pentiodide of Dafert.*<sup>1</sup>—This was obtained, following the plan given by that author, in crystals such as described by him, melting at about 85° C. (Dafert 89° C.) In analysis it gave 88.03 per cent. of total iodine, and 70.20 per cent. of iodine by titration (calculation for  $C_5H_5N.HI.I_4$ , total iodine 88.77 per cent., and superiodine 71.02 per cent.). For the titration the periodide was dissolved in alcohol, the end reaction was sharp, and the result conclusive as to the fundamental difference between the two compounds, one of which we believe to be a periodide of  $C_5H_5NH$ , and the other of  $C_5H_5N$ .

A hydrogen periodide of pyridine, therefore, like alkyl ammonium periodides in general, includes for each atom of nitrogen (in the molecule whatever its magnitude) just one atom of iodine which is left united to the nitrogen after the action of reducing agents of sufficient strength. On the contrary the periodides of pyridine not having ammonium hydrogen or alkyl contain no iodine left by such reducing agents in union with the base, as we say, no iodine firmly bound. Various forms of these two types may be represented as follows:

- (1)  $R_4NI.I_n$ , quarternary alkyl ammonium periodides.  
 $(R'''N)RI.I_n$ , quarternary pyridine periodides.  
 $(R'''N)HI.I_n$ , pyridine hydrogen periodide.
- (2)  $(R'''N).I_n$ , pyridine (amine) periodide.  
 $(R'''N)Br_3HBr$ , a superhalide (Grimaux).  
 $R_4PI.I_n$ , inferred by Masson and Kirkland.

#### ESTIMATIONS OF THE IODINE OF PERIODIDES.

1. The total iodine is obtained by precipitation as silver iodide, weighing this on filters to be described later.

<sup>1</sup> 1883: *Monatsh. Chem.*, 4, 508.

The sample is weighed, from a weighing bottle, by difference into a No. 2 beaker. About twenty cc. of a saturated solution of sulphurous acid is added, then a slight excess of silver nitrate solution (used of known strength). The mixture is heated on the water-bath for about an hour, breaking the crystals of periodide if necessary with a flat end of a glass rod, then acidulated strongly, using twenty to thirty cc. of nitric acid, (sp. gr. 1.20), and heated one to two hours or until the precipitate is of a uniform light straw color and the liquid perfectly clear. The precipitate is then put upon the prepared funnel of ascertained weight and washed, first with five per cent. nitric acid and then with hot water, using the pump throughout. The funnels are small sized "carbon tubes," the bottom loosely fitted with a glass plug or shoulder, on which is a layer of cracked glass, twelve to twenty mm. thick, made from beakers and sieved to pass a ten-mesh but not a twenty-mesh. After this is washed level, under pressure of the filter-pump, a layer of acid-washed asbestos is floated over it, and the whole dried at 130° to 150° C. for about two hours or for constant weight. Weighing is done with duplicate funnels, suspending them with an aluminum loop.

The washed silver iodide in the funnel is dried, with its duplicate (also wetted), for two hours at 130° to 150° C., or until weight is constant. A set of about thirty of the funnels have been in hand, and when all have been used, the asbestos layer and precipitate are carefully removed, and a fresh asbestos layer floated on, all which can be done for the set in about two hours.

Two to four parallel estimations have been made, and the average taken. The agreement of the estimations is fairly shown in these figures, quoted from the results: 86.69, 86.79, 86.84, 86.66; 72.45, 72.08, 72.45 ; 86.65, 86.29.

2. The iodine in excess of that for a normal iodide, that is, the iodine responding to reducing agents, has been estimated volumetrically by thiosulphate, using a solution of which one cc. equals 0.010 of iodine. To make this solution, "C. P. sodium thiosulphate" is recrystallized small by stirring while the solution cools. The volumetric solution is standardized by standard solution of potassium dichromate, which in turn is checked with one standardized with "chemically pure" iron wire. The dichro-

mate is purified by fusing a chemically pure article and pouring upon a tile. The factor of the thiosulphate solution is taken every two or three days. The periodide analyzed is weighed by difference, from a weighing bottle into a No. 3 beaker, taking 0.150 to 0.600 gram. Of alcohol from ten to fifteen cc. are added. All the periodides so far obtained are soluble in cold alcohol, but with much difference in the readiness and abundance of this solubility, and this property governs the speed of the estimation. The crystals can be broken under a flat end of a rod, and if not readily soluble, the titration is commenced before solution is completed, keeping down the excess of the iodine-like color. At the end starch can be used as an indicator, but after practice this is not necessary, as the extinction of the iodine-like color can be read to within one drop of the thiosulphate. The burettes had been calibrated and were used with a table of corrections. Other solvents have been tried but alcohol proves far the best for the crystals in titration. Two to four titrations have been made and the average given in each estimation. The agreement of the titrations is represented by a few quotations: of the pyridine methyl diiodide, 37.01, 37.24, 36.48, 37.17; pyridine methyl triiodide, 78.55, 78.84.

UNIVERSITY OF MICHIGAN.

## ON THE ANALYSIS OF ALLOYS OF LEAD, TIN, ANTIMONY AND ARSENIC.<sup>1</sup>

BY LAUNCELOT ANDREWS.

Received September 9, 1895.

THE experiments described in the present paper were carried out under my direction during the last winter by Mr. Earl Durfee. Part of them were suggested by Drown's investigation of the separation of tin from lead by repeated evaporations with concentrated hydrochloric acid, but were carried out previous to the publications of Jannasch,<sup>2</sup> and of Jannasch and Schmitt<sup>3</sup> on the same subject. All experiments referred to here, relate to the analysis of an alloy containing in round numbers eighty per cent. lead, thirteen per cent. antimony, seven per cent. tin. The exact composition of this metal will be given later.

<sup>1</sup> Read at the Springfield meeting.

<sup>2</sup> *Ber. d. chem. Ges.* 27, 3335.

<sup>3</sup> *Ztschr. anal. Chem.*, 9, 274.

## FIRST METHOD.

The attempt was made to drive off all tin and antimony as chlorides according to Drown. To this end one gram of the alloy was dissolved in aqua regia and evaporated to dryness, heating the residue to  $200^{\circ}\text{C}$ . The latter was moistened with about four cc. fuming hydrochloric acid and evaporated as before, the whole operation being repeated five times. The remaining lead chloride was, however, not free from tin and antimony. A series of attempts were then made to effect a separation by treating the alloy with bromine and hydrochloric acid gas, in varying forms of apparatus and at various temperatures. The details of these experiments need not be given, since they either failed to give a complete separation or were affected by practical faults of one kind or another.

On the other hand, no difficulty was found in completely volatilizing all the tin and antimony by heating the alloy directly, without previous solution, in a current of hydrochloric acid gas which had passed through concentrated nitric acid. The process was carried out as follows: Hydrochloric acid gas, evolved in a slow and steady stream by allowing the fuming acid to flow through a capillary tube into concentrated sulphuric acid, passes first through a flask containing ten cc. of nitric acid of 1.50 sp. gr., and then through a combustion tube of large diameter, thirty cm. long, containing a porcelain boat with the alloy in the form of turnings. The current of gas on leaving the combustion tube traverses a Volhard absorption flask, charged with a solution of potassium bromide and kept cold during the process. The combustion tube is covered with an asbestos tent and heated by means of an Argand burner to  $210^{\circ}\text{C}$ . The amount of the alloy used in each experiment was a half gram, and in two hours, during which time the operation required no attention whatever, the separation was complete and the snow-white residue in the boat was completely soluble in boiling water, while the distillate in the receiver was free from lead. The lead was weighed as sulphate. The receiver contained the antimony and tin and a little arsenic. To it was added the solution obtained by rinsing the unheated part of the combustion tube with hydrochloric acid. The small amount of arsenic present was easily separated from

the contents of the receiver by distillation according to Gooch and Phelps.<sup>1</sup> After the removal of the arsenic, tin and antimony were separated by Carnot's method,<sup>2</sup> which was found to be excellent.<sup>3</sup>

The process as described may be modified by attacking the alloy with nitric acid first, in a two-necked flask, then evaporating in a current of hydrochloric acid gas and heating in the same as before. The quantitative results are concordant, but the modified process is less convenient and requires decidedly more time.

## ANALYTICAL RESULTS.

	I. Gram.	II. Gram.	III. Per cent.	IV. Per cent.
Alloy taken .....	0.5000	0.5000	....	....
Lead sulphate.....	0.5849	0.5853	....	....
Lead found.....	0.3988	0.3991	79.75	79.82
Antimony trisulphide...	0.0925	0.0925	....	....
Antimony found .....	0.0661	0.0661	13.21	13.21
Stannic oxide .....	0.0434	0.0437	....	....
Tin found .....	0.0342	0.0344	6.84	6.88
Arsenic (volumetrically)	0.0006	0.0007	0.12	0.14
Total.....			99.92	100.05

## SECOND METHOD.

It has been observed that when various kinds of anti-friction metal or type metal were boiled with hydrobromic acid or with mixtures of hydrochloric acid and potassium bromide, the antimony remained undissolved, the arsenic distilled off and all the other constituents of the alloy went into solution. A more critical examination of the matter showed that, under the conditions named, in the presence of air, a small amount of the antimony dissolved, but that the undissolved portion was free from lead and tin. On the theory that the partial solution of the antimony was due to the oxidizing action of the air, it seemed likely that the addition of a powerful reducing agent, such as hydriodic acid, would prevent the loss of antimony, a view which was

<sup>1</sup> *Ztschr. anal. Chem.*, 7, 123.

<sup>2</sup> *Ztschr. anal. Chem.*, 88, 650.

<sup>3</sup> In this method, the solution, containing an oxalate and free oxalic acid and much ammonium chloride, is boiled with sodium thiosulphate. Beside the precautions given by the originator of the method, it is essential to success that the solution be boiled violently until one-fourth is boiled away, and that, finally, the acid be in excess as regards thiosulphate.

confirmed by an experiment in which potassium iodide took the place of the bromide.

One gram of the metal, in turnings, after boiling for one hour with hydrochloric acid of 1.10 sp. gr. and potassium iodide, (about one gram) was entirely disintegrated. The antimony remained undissolved as a dark gray powder. It was filtered from the boiling solution through a Gooch filter, washed with boiling water until free from lead iodide, dried, mixed with sulphur and gently ignited in a stream of carbon dioxide. This conversion into sulphide is needful because the finely divided antimony obstinately retains either water or hydrogen, in consequence of which the results come about seven-tenths per cent. too high if the metal is weighed directly.

## ANALYTICAL RESULTS.

	I.	II.
Metal taken.....	1.0000	1.0000 grams.
Antimony weighed direct....	0.1385	0.1375
Antimony trisulphide.....	0.1827	0.1833
Antimony calculated.....	0.1305	0.1310
Antimony .....	13.05	13.10 Per cent.

The subjoined table presents a summary of the results obtained by the different methods of analysis of the same alloy. Column I gives the results obtained by tedious but exact methods, not described in this paper but employed for a control. Column II gives the figures obtained by the first method above described. Column III those of the second method. Column IV the mean of all of the results.

## SUMMARY.

	I. Per cent.	II. Per cent.	III. Per cent.	Mean. Per cent.
Arsenic.....	0.13- 0.12	0.12	0.14- 0.13	0.128
Antimony.....	13.13-13.15	13.21-13.21	13.05-13.10	13.14
Tin .....	6.83- 6.84	6.84- 6.88	.....	6.85
Lead.....	79.87-79.95	79.75-79.82	.....	79.85
Total.....	99.97			

In conclusion, I wish to draw attention to a convenient device for maintaining temperatures lying between 200° and 500° which are difficult to secure with certainty by means of a Bunsen or even in some cases by the ordinary forms of air-bath. The

device consists simply of an ordinary Argand gas burner with chimney, as made for illuminating purposes, with the addition of a simple hood or tent of asbestos and sheet-iron to go over the top of the chimney and confine the heat. It is surprising what a wide range of temperatures this simple apparatus gives command of. It is very perfectly adapted for the ignition of antimonous sulphide in carbon dioxide, an operation which can be carried out with great nicety at  $400^{\circ}$ , but which is difficult and uncertain when a Bunsen burner is used as the source of heat. Many other operations, distillations, digestions, etc., are carried on advantageously in this way, the great merit of the arrangement consisting in the superior control of the temperature. It is, for example, well adapted to the conversion of calcium oxalate into carbonate.

### THE DETERMINATION OF GRAPHITE IN PIG-IRON.<sup>1</sup>

By P. W. SHIMER.

Received September 16, 1895.

THE purpose of this note is to call attention to a source of error in the determination of graphitic carbon, made by the usual method of solution in hydrochloric acid. Although the method is tedious, because of the necessary treatment of the separated carbon with caustic potash, alcohol and ether, the text-books seem to give it preference; and it is, perhaps, used more generally than the method of solution in dilute nitric acid. Solution in hydrochloric acid usually gives higher graphitic-carbon results than solution in nitric acid, and many, therefore, consider it more trustworthy, the inference being that the lower results obtained by nitric acid are due to the loss of some of the finely-divided graphite by reason of the oxidizing action of the solvent. But, experiments made in Dr. Drown's laboratory, about seventeen years ago, showed no appreciable oxidation of graphite in the fifteen or twenty minutes' boiling required for the solution of a sample of pig-iron.

The point I desire to bring out here is, that the high results in graphitic carbon obtained by solution in hydrochloric acid are due to the presence, in the graphitic residue, of titanium carbide,<sup>2</sup>

<sup>1</sup> To be read at the Atlanta meeting of the American Institute of Mining Engineers.

<sup>2</sup> See *Trans. Am. Inst. Min. Eng.*, 15, 455.

and possibly of other insoluble carbides, the carbon of which is, of course, included with the graphite in the final determination. In the nitric acid method, the titanium carbide is easily dissolved, and its carbon appears with the combined carbon, when the latter is determined by difference between graphitic and total carbon.

The method by solution in dilute sulphuric acid is open to the same objection as that by solution in hydrochloric acid; for titanium carbide is insoluble in sulphuric acid, and, I may add, it is also unattacked by hydrofluoric acid, and by a boiling solution of caustic potash.

The following is an analysis of a pig-iron unusually high in titanium:

	Per cent.
Silicon .....	3.650
Phosphorus .....	1.145
Sulphur .....	0.010
Manganese .....	0.226
Graphitic carbon .....	3.206
Combined carbon .....	0.128
Titanium .....	0.399
Iron (by difference) .....	91.236
	<hr/>
	100.000

The total carbon in this iron was determined by dissolving in an acidified solution of double chloride of copper and potassium, and subsequent combustion. The graphite was determined by solution in dilute nitric acid and combustion. A determination of graphite, made by solution in hydrochloric acid and combustion, gave 3.327 per cent. of graphite, a result 0.121 per cent. higher than that obtained by the nitric acid method. The amount of carbon combined as titanium carbide (TiC) with 0.399 per cent. of titanium is 0.1 per cent., which counts as graphite in the determination by solution in hydrochloric acid. The results may be set down as follows:

	Per cent.
Total carbon .....	3.334
Graphite by nitric acid solution .....	3.206
Graphite by hydrochloric acid solution .....	3.327

The error in the hydrochloric acid method falls heavily upon



the resultant estimate of combined carbon, which is determined by difference, as appears below :

	Per cent
Combined carbon, when graphite is determined by nitric acid	0.128
“ “ “ “ hydrochloric “	0.007

An experiment was made to determine the action of boiling nitric acid (1.20 sp. gr.) on the graphite from this iron. A sample of two grams was dissolved in hydrochloric acid (1.10 sp. gr). After washing the graphitic residue with water, it was boiled gently for one hour with nitric acid (1.20 sp. gr.), with the addition of a little water from time to time, to keep up the bulk of the solution. The graphite as thus determined, was 3.203 per cent. against 3.206 per cent., by direct solution in nitric acid, showing that the treatment, for one hour, with boiling nitric acid, had dissolved out the titanium carbide without having attacked the graphite. The graphite in this high silicon iron, however, was coarse and perhaps unusually resistant to the oxidizing action of nitric acid. It is proposed to make similar experiments on the graphite from a variety of pig-irons.

The 0.128 per cent. of combined carbon is made up as follows :

	Per cent.
Carbon combined with 0.399 per cent. titanium as TiC .....	0.100
Combined carbon soluble in hydrochloric acid (probably combined with iron and manganese) .....	0.007
Carbon possibly existing as insoluble carbide other than titanium carbide.....	0.021

A careful mechanical separation of a few grams of titanium carbide was made from several pounds of this iron by use of the long, slightly inclined glass plane described in the paper before the Institute referred to above.

Besides titanium and carbon in this separation, there is some vanadium, apparently also existing as an insoluble carbide, which would account for a part of the above 0.021 per cent. of combined carbon. This investigation is, however, still under way.

The writer has never encountered a pig-iron free from tita-

nium, the amount found varying usually from 0.05 to 0.40 per cent. In irons with a coarsely crystalline fracture, the cubical crystals of titanium carbide may always be found when carefully looked for. The conclusion seems to be fair that the hydrochloric acid method includes, with the graphite determined by it, the carbon existing as insoluble titanium carbide. With pig-irons containing from 0.05 to 0.40 per cent. of titanium, the graphite so determined will be from 0.013 to 0.100 per cent. too high, while the combined carbon will be correspondingly low.

It follows that more light would be thrown upon the condition of the carbon in pig-iron by making three determinations: *viz.*, one of total carbon, one of the carbon insoluble in hydrochloric acid, and one of graphite by the nitric acid method. We would thus have determinations of graphitic carbon; carbon combined with iron and manganese, soluble in hydrochloric acid; and carbon combined as carbides insoluble in hydrochloric acid. In high-silicon, low-sulphur titanic irons, the insoluble form of combined carbon exceeds the carbon existing as soluble carbides of iron and manganese. It is important to know how the carbon is combined. One-tenth per cent. of carbon combined with titanium in the condition of disseminated microscopic crystals, probably has no effect on the hardness of pig-iron; while the same amount of carbon, combined with iron and manganese, would have an appreciable hardening effect. Practically, therefore, it may be desirable to have the carbon existing as carbides insoluble in hydrochloric acid appear with the graphite as determined by the hydrochloric acid method, although the actual graphite can be determined only by solution in nitric acid. At all events it is essential to know by what method graphite has been determined, in order to draw conclusions from determinations of graphitic and combined carbon in pig-iron.

## ON THE COMPOSITION OF PELAGINE.

BY A. B. GRIFFITH AND CHARLES PLATT.

Received October 7, 1895.

THE chemical composition and constitution of the violet pigment of Pelagia (one of the Medusae) has been established by us, as follows: By treatment with hot alcohol and ether the pigment and fats are dissolved and the solution, after filtration, is evaporated carefully to dryness. The residue is treated with a solution of sodium hydroxide and the pigment then rapidly extracted by means of carbon disulphide. Upon the spontaneous evaporation of the solvent, the violet pigment is obtained as an amorphous residue.

Analysis of this pigment gave the following results:

I.	Substance employed .....	0.2058	gram.
	Carbon dioxide .....	0.47325	"
	Water.....	0.0810	"
II.	Substance employed.....	0.4605	"
	Nitrogen.....	15.15	cc.
	Barometric reading .....	742.	mm.
	Temperature.....	15°	

Reduced to percentages and calculating the formula the following results are obtained:

	I.	II.	Calculated for $C_{30}H_{17}NO_7$ .
Carbon .....	62.71	....	62.66
Hydrogen.....	4.38	....	4.43
Nitrogen.....	....	3.75	3.66
Oxygen .....	....	....	29.24

Analysis, then, would indicate the formula  $C_{30}H_{17}NO_7$ . Pelagine is soluble in alcohol, in ether, and in acetic acid; it is insoluble in water, but it is very soluble in carbon disulphide. Solutions of the pigment are decolorized by exposure to light and, on spectroscopic examination, do not yield characteristic absorption bands. It has, apparently, no respiratory function and probably belongs to the same order of pigments as tetronerythrin,<sup>1</sup> rhodopsin, etc.; in other words, pelagine is probably a lipochrome or a nitrogenous derivative of that class. In certain respects it may be said to resemble melaine, the pigment of Sepia, investigated by Girod, Variot, and Desfosses.<sup>2</sup>

<sup>1</sup> *Compt. rend.*, 93, 1029.

<sup>2</sup> *Compt. rend.*, 93, 97.

## ON THE VOLUMETRIC DETERMINATION OF TITANIC ACID AND IRON IN ORES.

BY H. L. WELLS AND W. L. MITCHELL.

Received July 22, 1895.

THE difficulties connected with the gravimetric determination of titanic acid make a reliable volumetric method very desirable, especially for the analysis of titanic iron ores. We have therefore turned our attention to this subject and have found that satisfactory results can be obtained by a slight modification of a process which has long been known.

About thirty years ago, F. Pisani<sup>1</sup> stated that the acid under consideration could be determined by reduction with zinc in hydrochloric acid solution, using a gentle heat, and when the violet color no longer deepened, pouring off the liquid from the remaining zinc and titrating with potassium permanganate. Pisani gave no test analyses, and, since his process has not been generally adopted, it is evident that it has not proved satisfactory in the hands of others.

A number of years ago one of us (Wells) had occasion to analyze a large number of titanic iron ores and attempted to use Pisani's method with the use of sulphuric acid instead of hydrochloric acid, as recommended by the originator of the process. This modification was made on account of the well-known interference of chlorides with the permanganate method, and it was found that the difficulty mentioned by Pisani, that titanic acid was liable to be precipitated by heating sulphate solutions, could be readily overcome by using a sufficiently large quantity of sulphuric acid. The results of a great many trials at that time, however, showed that the method gave very low results, and the process was then abandoned. The process used in the experiments just referred to was precisely the same as that which we now recommend and which will be described in detail below, except that after reduction with zinc the solution was poured off, from the excess of that metal, into a beaker for titration, an operation which Pisani recommended, and which is customary in the determination of iron by this method. It is now evident that the failure of the method was due to the contact of

<sup>1</sup> *Compt. rend.*, 59, 289.

the solutions with atmospheric air, for, while ferrous sulphate is acted upon very slowly, the sulphate corresponding to the lower oxide of titanium is very rapidly oxidized under such circumstances.

Marignac,<sup>1</sup> with his accustomed skill, applied Pisani's method, soon after its publication, to the determination of titanic acid in the presence of niobic acid. He was obliged to use special conditions in order to avoid the reduction of the other acid at the same time, but the feature of his process which is interesting in the present connection is that he reduced the titanic acid by means of a long rod of pure zinc extending up into the neck of the flask which held the solution, and, after allowing the reduction to take place out of contact with air, he finally took out the zinc and titrated directly in the flask without transferring. Marignac gave a number of test analyses which showed that the method gave very good results, although they were a little too low with the larger quantities of titanic acid used.

We have modified the method of Pisani as improved by Marignac by using sulphuric acid solutions and by protecting the liquid during cooling and titration by means of carbon dioxide, and we have also arranged the process for the determination of iron along with the titanic acid. The details of the operation are as follows:

Five grams of very finely pulverized ore are placed in a rather large beaker covered with a watch-glass and treated with about 100 cc. of concentrated hydrochloric acid. A very gentle, gradually increasing heat is applied for several hours, more hydrochloric acid is added if necessary, and when no further action is apparent about fifty cc. of a mixture of equal volumes of concentrated sulphuric acid and water are added and the whole is evaporated until the sulphuric acid fumes strongly. After cooling, about 200 cc. of water are added, the whole is heated until the sulphates are dissolved, and the liquid is filtered into a liter flask. With many titanic ores this operation will have dissolved everything except silicious matter. If, however, some undissolved ore remains, it is ignited, to burn the filter-paper, in a platinum crucible, and the residue is fused with potassium

<sup>1</sup> *Ztschr. anal. Chem.*, 7, 112.

disulphate, at a gradually increasing heat, up to low redness, until the black particles have disappeared. To the cake in the crucible several volumes of concentrated sulphuric acid are added, heat is gradually applied until the whole becomes liquid, then this is heated with a moderate volume of water to dissolve the sulphates, and the liquid is added to the main solution in the liter flask. Filtration may be omitted here, or in the case of the original solution, provided that the silicious matter is not to be weighed.

The liquid in the liter flask is diluted to the mark and mixed, and four portions of 200 cc. each, representing one gram of ore, are taken, two of them into Erlenmeyer (conical) flasks of 500 cc. capacity, and the other two into ordinary flasks of 350 cc. capacity.

To determine iron, hydrogen sulphide is passed into the solutions in the ordinary flasks until they are saturated with the gas, then inverted porcelain crucible covers are placed upon the mouths of the flasks and the solutions are heated and boiled continuously, so that air cannot enter, until the hydrogen sulphide has been completely removed. This point can be determined by testing the escaping steam with paper which has been dipped in a solution of lead acetate made strongly alkaline with potassium hydroxide. The flasks are then quickly filled to the neck with cold distilled water which has been recently boiled, best by means of an inverted wash-bottle, directing the stream against the neck of the flask in such a way that the water does not mix to a great extent with the heavier sulphuric acid solution. If the stream of cold water does not strike the top of the neck, there is little danger of breaking the hot glass. The contents of the flasks are now rapidly cooled by means of a stream of water, transferred to large beakers, and titrated with potassium permanganate solution.

To the solutions in the Erlenmeyer flasks about twenty-five cc. of concentrated sulphuric acid are added, then in each case three or four rods of chemically pure zinc, about fifty mm. long and six or seven mm. in diameter, are attached to the loop of a porcelain crucible cover, which is larger than the mouth of the flask, by means of platinum wire wound securely around them

near the middle. The length of the wire is so arranged that the pieces of zinc will be suspended in the liquid when the cover is placed on the flask. When this has been accomplished the liquid is boiled gently, so as to keep out air, for thirty or forty minutes, then, without interrupting the boiling, a glass tube, so bent that it extends fifty mm. or more into the flask, which is delivering a rather rapid stream of carbon dioxide, is introduced under the cover. Care should be taken to have the carbon dioxide free from air, and that hydrochloric acid which contains sulphur dioxide is not used for its generation. The flask is now rapidly cooled, and then the zinc is washed with a jet of water and removed, and the solution is titrated with permanganate in the flask while the carbon dioxide is still being passed in. The difference between the permanganate used in this case and that used for the iron alone, represents the amount corresponding to the titanic acid. The factor for metallic iron divided by 0.7 gives the factor for titanic acid ( $\text{TiO}_2$ ).

When a fifty cc. burette is used, the most convenient strength for the permanganate solution is when one cc. is equal to about 0.014 grams of metallic iron, corresponding to seven and nine-tenths grams of potassium permanganate per liter.

It is customary in this laboratory to standardize permanganate solutions by a method which very closely approaches the one described above for the actual determination of iron, so that, if any slight errors are inherent in the process, they are likely to be eliminated because they have an equal effect upon the standardization and the determination. The method is simple and convenient, and a large amount of experience has shown it to be very accurate. To carry out this operation, a 350 cc. flask is half filled with sulphuric acid, (the strong acid diluted with about eight volumes of water). This is heated to boiling with an inverted crucible cover upon the mouth of the flask, and after the air has been expelled, about six-tenths gram of the purest iron wire, representing nearly the average amount of iron in one gram of an ore, is dropped in and gentle boiling is continued until it has dissolved. The flask is filled to the neck with water, cooled and finally the liquid is transferred to a beaker and titrated.

The method of determining iron by reduction with hydrogen sulphide, although well known, does not appear to be as generally used as it deserves to be. The precipitated sulphur present in the liquid has absolutely no effect upon cold permanganate solution, but precipitated sulphides, such as copper sulphide, should be filtered off before boiling. Since concentrated sulphuric acid is an oxidizing agent, care must be taken to use sufficiently dilute solution, and not boil them down until the acid becomes strong.

We have made some test analyses upon the method of determining titanic acid volumetrically. Crude potassium titanofluoride,  $K_2TiF_6$ , was recrystallized twice from water and used as the source of titanium. Weighed quantities of the carefully dried salt were evaporated with sulphuric acid, and the resulting substance was treated essentially as has been described above, but with some variations in the time of boiling, the strength of the acid and the amount of zinc used. The following table gives the results obtained in grams :

Potassium titanofluoride taken.	Titanium found.	Titanium calculated.	Error.
0.7638	0.1437	0.1527	—0.0090
0.6425	0.1225	0.1285	—0.0060
0.7778	0.1524	0.1555	—0.0031
0.6793	0.1308	0.1358	—0.0050
0.8226	0.1607	0.1645	—0.0038
1.0956	0.2107	0.2191	—0.0084
0.4451	0.0848	0.0890	—0.0042
0.6359	0.1215	0.1271	—0.0056
0.9004	0.1715	0.1800	—0.0085
0.4634	0.0882	0.0926	—0.0044

The results show a fair degree of uniformity, but they are invariably too low. A part of the deficiency was probably due to the impurities in the potassium titanofluoride used, for it is quite possible that certain impurities may have been increased rather than diminished by recrystallizing it, and it is exceedingly difficult to obtain any titanium compound that is certainly free from all other acid-forming elements. The greater portion of the error was doubtless due to the action of air which gained access to the liquid in spite of the precautions used, and it is evident that the accuracy of determinations made by this method



would be increased by adding one-twentieth or one-thirtieth to the amount of titanio acid found under the conditions that we have used.

The great influence of the action of air is shown by two determinations which were made exactly like those given in the above table, except that, after cooling in carbon dioxide, the solutions were transferred to beakers and titrated as quickly as possible.

Potassium titanofluoride taken	Titanium Found.	Titanium calculated.	Error.
0.6831	0.1078	0.1366	0.0288
0.9545	0.1535	0.1909	0.0374

The volumetric method, even without correction, will be likely to give more reliable results than those obtained by gravimetric determination, unless great care and skill are displayed in carrying out the latter.

SHEFFIELD SCIENTIFIC SCHOOL,  
NEW HAVEN, CONN.

## ARSENIC IN GLYCEROL.<sup>1</sup>

BY G. E. BARTON.

Received September 9, 1895.

IN following up the literature of glycerol I find that the first to note the presence of arsenic in the medicinal article was Jahns,<sup>2</sup> but he apparently did not investigate the subject thoroughly.

E. Ritsert<sup>3</sup> was the next to take the subject up. He showed the presence of arsenic in seven samples of medicinal glycerol, by the following test, which he says shows 0.001 mg. in one cc. while the Marsh test shows only 0.01 mg. in one cc. One cc. of glycerol is placed in a small measuring cylinder and to this one cc. of water is added, together with fifteen drops of hydrochloric acid and 0.6 gram zinc. The top of the cylinder is covered with filter-paper, moistened with a 1 : 1 silver nitrate solution or saturated mercuric chloride solution, and a yellow stain is obtained on the paper if arsenic is present. Ritsert also states that ammoniacal silver nitrate solution is a good reagent for arsenious acid and that the arsenious acid present probably

<sup>1</sup> Read at the Springfield Meeting.

<sup>2</sup> Pharm. Ztg., 1888, 652.

<sup>3</sup> Pharm. Ztg., 1888, 715, and 1889, 104, 360 and 625.

explains the difference in the indications given by litmus and phenolphthalein as observed by him. He gives as the probable source of the arsenic found, the sulphuric acid used in the course of manufacture. Issue is taken with G. B. Smith,<sup>1</sup> who states that glycerol itself reduces silver nitrate, and hence ammonio-silver nitrate can not be used to detect arsenic.

An abstract of an article by G. Vulpius<sup>2</sup> gives the cost of an article free from arsenic as ten per cent. more than the current price.

L. Siebold<sup>3</sup> on "Arsenic in Glycerol," finds from one in 4000 to one in 6000 parts of arsenious acid in glycerol used for perfuming and medicinal purposes, and in one case one part in 2500 parts. All glycerols free from arsenic were traced to one process described as that "by which as a rule glycerol used for dispensing purposes is understood to be made." He ascribes the presence of arsenic in some cases to the solution of the arsenic present in the glass of the bottle, but this has never been confirmed and hardly seems probable.

Dr. Benno Jaffé<sup>4</sup> attacks the ammonio silver nitrate test which he claims to be of no value as it does not give constant results, either for arsenic or acrolein and similar bodies.

J. Luttké,<sup>5</sup> after an elaborate examination of twenty-one samples confirms Jaffé's conclusions and points out as among the disturbing causes, chlorides and organic acids.

There can be no doubt of the presence of arsenic in some glycerol, but I have found no one except Siebold who has attempted to give any idea of the quantity, and while he does not give the method used in obtaining the results stated, I infer from the text that, using either silver nitrate or mercuric chloride to absorb the hydrogen arsenide, he has compared the depth of color obtained with that given by known quantities of arsenious acid. A few experiments led me to think that this cannot be a very accurate method at best, so I set about to apply the method given by Sanger, for the estimation of arsenic in wall paper,<sup>6</sup> which

<sup>1</sup> Ned. Tijdschr. v. Pharm., 1889, 143.

<sup>2</sup> Apoth. Zeit., 1889, 4, 439; *J. Soc. Chem. Ind.*, 8, 639.

<sup>3</sup> Pharm. J. Trans. [3], 20, 205.

<sup>4</sup> Chem. Ztg., 1890, 14, 1493.

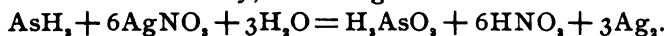
<sup>5</sup> Apoth. Ztg., 1891, 6, 263.

<sup>6</sup> Proc. Amer. Acad., 26, 24.

consists of comparing the mirrors obtained in a modified form of the Marsh apparatus with those prepared from known quantities of arsenious oxide in solution as sodium arsenite.

The apparatus as described by Sanger consists of a constant hydrogen generator, filled with chemically pure sulphuric acid and zinc, a smaller reduction flask having a thistle tube for introducing acid and solutions to be treated and which of course contains a small amount of chemically pure acid and zinc, a drying tube containing calcium chloride, and finally a reduction tube in which the mirror is obtained.

The cost of using chemically pure acid and zinc in the constant hydrogen generator would of course be great, and the first point I turned my attention to was a method for purifying the hydrogen generated by impure acid and zinc so that the constant generator could be run at a reasonable cost. I found that by passing the hydrogen through silver nitrate solution, the arsenic was removed entirely, according to the well-known reaction:



Another improvement in the apparatus as I used it was the substitution of a small separating funnel for the thistle tube in the reduction flask. This prevented the escape of any gas at that point while the former arrangement allowed a variable quantity to escape.

The apparatus as finally used in this work, consisted of a constant hydrogen generator, using impure acid and zinc, a wash bottle containing silver nitrate solution, a wash bottle containing water to remove any traces of silver nitrate solution which the gas might carry mechanically and which would otherwise hold back some of the arsenic in the reduction flask, a reduction flask, with separating funnel as before described, a drying tube containing calcium chloride, and finally the reduction tube.

The efficiency of the silver nitrate solution was proven by running over one hundred hours without obtaining a mirror, whereas a mirror could be obtained in from five to ten minutes from the same hydrogen not passed through silver nitrate. Using the ordinary acid and zinc of the laboratory, I found an amount of silver nitrate solution representing one gram of the salt prevented the formation of a mirror for over two hundred hours.

The mode of operating did not differ essentially from that described by Sanger. The apparatus was first filled with hydrogen, the reduction flask containing at this time only the pure zinc, of which about three grams were used. The jet at the end of the reduction tube was then lit and the tube heated at the proper place, after which a little sulphuric acid was introduced into the reduction flask and the action allowed to go on for a few minutes to prove the purity of the reagents. The solution to be treated was then added and washed in by more acid, or water where the glycerol was added directly to the flask.

The acid used was about one to eight and by slightly varying these proportions it was found possible to get along without cooling the flask. No two samples of zinc were found to contain the same amount of carbon or at least to dissolve with the same rapidity so that a careful adjustment of the acid is necessary for each lot and as large an amount as possible should be granulated at one time. It is also necessary to have standard mirrors made at different speeds to counterbalance the slight differences which are unavoidable.

The calcium chloride tube should be carefully looked after in order that the gas may be perfectly dry. I have found it best to ignite the article furnished by the makers before using. It is also a good plan to attach the bellows and blow through it a few moments after filling, to remove any slight amount of dust that might otherwise be carried into the reduction tube.

The glass used for the reduction tube should be of the hardest obtainable. I have found great variations in different pieces of the same lot. It would be of advantage if glass were carefully selected, and if necessary carefully tested, could be quoted by dealers, as otherwise a large amount of tubing is accumulated too hard for ordinary work but not hard enough for this purpose. Great care should always be taken to get tubes uniform at the point of deposition and in spite of this it was found necessary to have several mirrors of each grade.

A small white mirror was found to form beyond the arsenic mirror in those tubes representing small amounts but in those obtained from larger amounts either wholly or partly coinciding. In the latter case the arsenic mirror took on a totally different

color, the characteristic brown of the pure arsenic mirror becoming black. This mirror was without doubt in some cases partly due to moisture, and showed minute drops when examined under a lens. It also seemed to be less with the harder glasses. After having used fresh calcium chloride and the hardest glass obtainable, the only resource is in having standard mirrors representing all possible variations.

Another trouble was found to be the deposition of the arsenic in two mirrors entirely apart. This Gooch and Moseley<sup>1</sup> suggest to be due to the formation of two allotropic forms of arsenic by the too high heating of the reduction tube. They avoid this by enclosing the reduction tube in an iron or nickel jacket. Here again several mirrors of each standard amount are a remedy.

Having obtained a sufficient number of standard mirrors eight samples of glycerol, such as is ordinarily sold by the druggists of this city were procured. Six represented the best American makers and two were imported.

Five grams of each sample were treated with five cc. of a mixture of thirty parts sulphuric acid and one part nitric acid and the mixture heated carefully with constant stirring till a dry charred mass giving off sulphur dioxide was obtained. This was then allowed to cool and about ten cc. of water added and then the mass again heated till sulphur dioxide was given off. After cooling about fifteen cc. of water was added and the mixture boiled vigorously to expel sulphur dioxide. The liquid was then filtered off and water added as before, boiled and again filtered. This was repeated twice to insure the complete extraction of the arsenic from the charred mass. The solution thus obtained was added to the reduction flask and the usual process carried out. Five of the eight samples showed arsenic in variable amounts.

To prove that arsenic, if present, would be shown by this course of manipulation, five grams of glycerol showing no arsenic were weighed out and one cc. of an arsenic solution added. This mixture was treated exactly as the other samples had been and no arsenic mirror obtained. From this and the comparison

<sup>1</sup> Am. J. Sci., 48, 294.

of these mirrors with those obtained by other processes, I concluded that some, at least of the samples contain, or are decomposed into something capable of holding black arsenic. This leads to the query: What is the effect of the combined glycerol present in the toxicological examination for arsenic? May not the trouble with the glycerol be due to a decomposition product which would also be formed in the supposed case? I have not had time to investigate this important point.

Five grams of the same glycerol used in the previous experiment were then added direct to the reduction flask after diluting with water and arsenic in small quantities was obtained. One cc. of the arsenic solution was then added to the glycerol and, after diluting, the reduction carried out at once as in the previous experiment and an amount of arsenic equal to that in the one cc. of solution and five grams of glycerol, obtained. After trying several plans this method was finally chosen as both the quickest and most accurate.

The following quantities of arsenious oxide ( $As_2O_3$ ) were obtained in the eight samples:

No.		No.	
1	..... trace.	5	..... faint trace.
2	..... 0.08 mg.	6	..... trace.
3	..... faint trace.	7	..... 0.004 mg.
4	..... none.	8	..... 0.003 mg.

To prove that the mirrors obtained were due to arsenic and nothing else, mirrors were heated gently and moist hydrogen sulphide passed through them. In this manner part of the arsenic was changed to the yellow sulphide. Some of the gas from the reduction flask was passed into silver nitrate solution and a black precipitate of metallic silver obtained. On carefully neutralizing with ammonium hydroxide a yellow precipitate of silver arsenite, soluble in excess, and also in nitric acid was obtained. The nitric acid solution was precipitated with hydrochloric acid, a clean copper wire added and the solution warmed. A grey coating formed on the copper. Blank experiments showed the reagents to be pure.

From the above there can be no doubt but that arsenic was present in the glycerols examined.

The method mentioned by several authors, namely, diluting

the glycerol with an equal volume of water, adding hydrochloric acid and then metallic zinc, and obtaining a yellow coloration on a filter-paper moistened with either silver nitrate solution (1 : 1) or saturated mercuric chloride solution was tried. A twenty-five cc. measuring cylinder was used and the paper fastened tightly over the mouth, the gas escaping at the nose. In this manner using the silver nitrate solution the test was found to be about five times as delicate as the Marsh test used, and a trace of arsenic was found in sample No. 4, which had shown none in the Marsh test. The coloration was not permanent enough, owing to the action of light and other causes to be compared with standards made with permanent coloring-matters. The test with mercuric chloride, carried out in the same way, was not quite as delicate as the Marsh test. It would hardly be possible by comparing with standards to make this a quantitative method as accurate as the Sanger-Berzelius-Marsh test. It is to be noted that sample No. 2, which showed the largest amount, contained 0.08 arsenious oxide or one part in 62500, while Siebold reports as much as one part in 2500 in one case. Seventy mg. is the smallest dose known to have produced death according to Tanner<sup>1</sup> which would be equivalent to the amount in over four liters of glycerol No. 2, or to 150 cc. of Siebold's worst sample. Although arsenic is slowly eliminated from the system, still it would be quite possible by the indiscriminate use of sample No. 2, for some time, to accumulate enough in the system to cause death. Certainly the above figures are worthy of note by persons using glycerol for medicinal purposes.

So-called C. P. glycerol is often recovered from the waste products of the soap manufactories, and in this case the presence of arsenic is accounted for as follows: Starting with arsenical oil of vitriol, the arsenic is changed in the hydrochloric acid still to the chloride, which distils over with the acid. On neutralizing the spent lyes with hydrochloric acid the arsenic remains in the solution and is repeatedly distilled over with the glycerol.

In this connection I may say that I found no hydrochloric acid in this laboratory free from arsenic as shown by the yellow stain in the silver nitrate test, but had no trouble in preparing such

<sup>1</sup> Memoranda of Poisons, p. 69.

an article from chemically pure sulphuric acid which I had proven to contain no arsenic.

In conclusion I take pleasure in acknowledging my deep indebtedness to Dr. Charles E. Munroe for his many suggestions.

THE COLUMBIAN UNIVERSITY,  
WASHINGTON, D. C.

## THE OCCURRENCE OF TRIMETHYLENE GLYCOL AS A BY-PRODUCT IN THE GLYCEROL MANUFACTURE.<sup>1</sup>

BY ARTHUR A. NOYES AND WILLARD H. WATKINS.

Received September 9, 1895.

**D**URING the past winter our attention was called to an unusual difficulty experienced by one of the soap-making firms in the neighborhood of Boston in obtaining their glycerol of the required commercial gravity. The information furnished in regard to it indicated the presence in the glycerol of some uncommon impurity, and a considerable quantity of the "light stuff" having been generously placed at our disposal by the soap company, we were enabled to investigate it. It was submitted to fractional distillation, first at diminished and then at ordinary pressure, and a liquid boiling between  $214^{\circ}$  and  $217^{\circ}$  at 760 mm. pressure was thus separated from it. This liquid was found to have a specific gravity of 1.056 at  $\frac{1}{2}^{\circ}$ , and gave the following results on analysis:

0.2293 gram substance gave 0.3998 gram carbon dioxide and 0.2158 gram water.

	Found.	Calculated for $C_3H_8O_3$ .
Carbon .....	47.5 <sup>1</sup>	47.37
Hydrogen .....	10.46	10.53

The substance is therefore trimethylene glycol, which has a boiling-point of  $214^{\circ}$  and a specific gravity at  $\frac{1}{6}^{\circ}$  of 1.0526. The isomeric propylene glycol boils at  $188^{\circ}$ – $189^{\circ}$  and has a specific gravity of 1.0403 at  $\frac{1}{6}^{\circ}$ . The "light stuff" contained a very considerable proportion, about thirty-eight per cent. of glycol.

The origin of the glycol is a matter of considerable interest. There is little doubt that it was produced by fermentation of the

<sup>1</sup> Read at the springfield meeting.



glycerol. For it has already been shown by Freund<sup>1</sup> that trimethylene glycol is, in fact, one of the principal fermentation products of that substance. It is moreover highly probable that the glycol was present in the fat before saponification by the alkali, as the fermentation can hardly have taken place in the soap lye, both on account of its saline character, and on account of the short time intervening between the saponification and the recovery of the glycerol. It had probably been produced in the fat by spontaneous saponification and subsequent fermentation of the glycerol.<sup>2</sup> Refuse house fat formed a considerable part of the soap stock.

The presence of the glycol in glycerol used for making nitroglycerol might be a source of danger, since it reacts with nitric acid with explosive violence. Its presence would be detected in the usual examination by a low specific gravity accompanied by a high oxidation equivalent as shown by the bichromate titration.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,  
BOSTON, MASS.

## THE EVOLUTION METHOD FOR THE DETERMINATION OF SULPHUR IN WHITE CAST-IRON.<sup>3</sup>

BY FRANCIS C. PHILLIPS.

Received September 9, 1895.

THIS method is based upon the assumption that when iron is dissolved in an acid any sulphur that may occur in the iron unites with the escaping hydrogen, forming hydrogen sulphide. In the usual mode of conducting the process the impure hydrogen evolved is led into a suitable absorbent and the sulphur finally determined, either by oxidation and precipitation as barium sulphate, or by a volumetric method. In applying the process Fresenius<sup>4</sup> directs that the iron be dissolved in *dilute* hydrochloric acid. Von Reis<sup>5</sup> and Blair<sup>6</sup> concur in this recommendation, as does also Dudley in

<sup>1</sup> Monatsh. Chem., 2, 638.

<sup>2</sup> Mr. E. Twitchell of Cincinnati informs us that he has found the glycol present in considerable quantity in the "tank liquor" separating from the fat before saponification.

<sup>3</sup> Read at the Springfield meeting.

<sup>4</sup> Quant. Analyse, 1877, 428.

<sup>5</sup> Stahl-eisen, 1894, 963.

<sup>6</sup> Chemical analysis of Iron, p. 54.

the published directions for the determination of sulphur in cast-iron, issued by the Pennsylvania Railroad Company.

For the absorption of the hydrogen sulphide various reagents have been recommended. Johnson<sup>1</sup> proposed the use of a bromine solution. Blair absorbs the hydrogen sulphide in an alkaline solution of lead acetate, oxidizes the resulting lead sulphide, and precipitates the sulphuric acid as barium sulphate. According to the usage at many iron works the gases are led into an ammoniacal cadmium chloride solution which is afterwards acidulated and the sulphur determined volumetrically by standard iodine. In order to complete the expulsion of the hydrogen sulphide from the solution of ferrous chloride a stream of carbon dioxide has been generally employed. Blair uses for this purpose a current of hydrogen, while Dudley states that neither gas has any advantages over air used in a slow stream. In iron-works laboratories it is a generally recognized fact that in the use of the evolution method for certain cast-irons, notably those containing a high percentage of combined carbon, an error is liable to occur, and in cases where great accuracy is required the aqua regia method is usually preferred.

It is common to find that during the solution of cast-iron in an acid there is produced a considerable quantity of strong smelling gaseous hydrocarbons. The interior surface of the flask becomes coated with minute drops of an oily liquid which adheres to the glass and is not miscible with water. There can be little doubt that the loss of sulphur which often results in its determination by the evolution method is dependent largely upon the formation of these organic compounds during the solution of the iron.

It is common to find that the white irons dissolve in acid leaving a nearly white silicious residue of a somewhat flocculent character. This residue contains a varying amount of sulphur, which is insufficient, however, to account for the low results sometimes obtained in the determination.

It has been attempted to explain the error on the hypothesis that sulphur exists in iron in more than one modification, that that portion of the sulphur which occurs in the ordinary form

<sup>1</sup> *Ztschr. anal. Chem.*, 1874.

passes readily into hydrogen sulphide on its elimination from the iron by the action of the hydrochloric acid, while another portion existing in some unknown modification, is not converted into hydrogen sulphide, but remains passively in the residue and is thus lost in the determination.

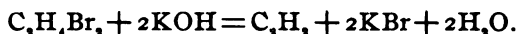
Such an assumption involves a difficulty. It is not usually considered necessary in order to explain the chemical changes undergone by the elements of a compound to suppose that the atoms of carbon, hydrogen or sulphur exist in the compound in forms different from those in which we know them in other compounds. Of the six hydrogen atoms in alcohol one differs from the others as to its behavior towards oxidizing agents. The supposition that there are two allotropic forms of hydrogen in alcohol would hardly be accepted, however, for it is commonly believed to be the mode of linking of the atoms rather than the occurrence of the elements in allotropic forms in the compound that determines the nature of chemical changes. The fact that a portion only of the sulphur in white cast-iron is liberated as hydrogen sulphide by an acid suggests that the molecule of cast-iron does not contain all its sulphur linked in the same manner. In the present paper I have described some experiments undertaken in order to study the reactions of the evolution method more fully. For the purpose in view a white iron containing 0.17 per cent. of sulphur, as found by the aqua regia method was used.

*Experiment 1.*—Four grams of this iron were dissolved in hydrochloric acid of 1.12 sp. gr. As the process of solution became retarded the acid was heated gradually to the boiling-point. The escaping gas was led into a solution of bromine. A small quantity of a heavy oil collected in the bromine solution. This oil was decanted, introduced into a platinum boat and burnt in a porcelain tube in a current of nitrous oxide gas. The gas escaping from the tube was led into bromine water, which on treatment with barium chloride in the usual way yielded a precipitate of barium sulphate, showing that the original oil had contained sulphur.

*Experiment 2.*—The oil collected in an experiment similar to the preceding was digested with concentrated nitric acid. The

mixture, contained in a glass-stoppered bottle, was kept at a temperature of  $100^{\circ}$  C. for two hours. On one evaporation to dryness, re-solution of the residue in water, and addition of barium chloride no precipitation occurred. The solution was then evaporated again to dryness with addition of some barium nitrate, and the residue heated to redness. On re-solution in water a precipitate of barium sulphate appeared. This experiment showed that the oil contained sulphur but in a form not easily oxidizable directly to sulphuric acid by bromine water or concentrated nitric acid. The fact that a precipitate of barium sulphate was not obtained by mere evaporation with strong nitric acid, but was quickly produced on ignition of the evaporated residue and re-solution in water, indicated the possible presence of a sulphur ether of the type  $(CH_3)_2S$ .

*Experiment 3.*—That the oil condensed in the bromine flask was not a pure sulphur compound was evident from the following experiment: A few drops of the oil were warmed in a flask with an alcoholic solution of potassium hydroxide. The escaping gas was found to yield a red precipitate in an ammoniacal solution of cuprous chloride, indicating acetylene. From this it seemed probable that the oil found in the bromine solution consisted mainly of ethylene dibromide, which on treatment with the alcoholic potash had yielded acetylene by the reaction



*Experiment 4.*—The flask which had been used for a sulphur determination by the evolution method, and which exhibited minute oil drops on its inner sides, was rinsed with alcohol and with chloroform. The combined liquids were evaporated in a platinum boat in which a minute quantity of a residue was left. On strongly heating in nitrous oxide and passing the products into bromine water a precipitate of barium sulphate was obtained after the usual treatment with barium chloride.

*Experiment 5.*—The silicious residue left from the solution of the iron in hydrochloric acid in the determination of sulphur by the evolution method was found on fusion with alkaline carbonate and nitrate to yield a small quantity of barium sulphate when treated in the usual manner for the determination of sul-

phuric acid. It seemed still to be of importance to ascertain whether the sulphur in this residue existed as a metallic sulphide or as an organic compound. The possibility of the presence of free sulphur seemed to be excluded, inasmuch as air had been expelled from the flask during the solution of the iron by a stream of carbon dioxide. Accordingly, the silicious residue from a sulphur determination was dried at a gentle heat and extracted after the fashion of an ordinary fat extraction process by boiling alcohol and afterwards by boiling chloroform. The extract, on evaporation, left a trace of a yellow oil. This oil, on being burnt in nitrous oxide, gave indications of the presence of sulphur when tested in the manner already described.

The silicious residue, after extracting with alcohol and chloroform, was found, on fusion with alkaline carbonate and separation of the silica, not to contain sulphur. From this it appeared that the silicious residue contained an organic sulphur compound, but did not contain a metallic sulphide.

The acid solution of ferrous chloride left in the evolution flask was filtered, agitated with a few cc. of chloroform. The chloroform on evaporation, ignition of the residue in nitrous oxide, and the usual treatment, was shown to contain sulphur.

The following determinations were made in the manner indicated. The percentages of sulphur are based upon the weight of the iron dissolved.

	Per cent.
1. Sulphur from oil collected in bromine solution....	0.008
2. Sulphur obtained from alcohol and chloroform rinsings of flask.....	0.010
3. Sulphur extracted from silicious residue.....	0.013
4. Sulphur obtained by <i>fusion</i> of silicious residue after extracting by alcohol and chloroform.....	0.000
5. Sulphur obtained by agitation of the filtered ferrous chloride solution with chloroform, representing therefore organic sulphur compounds held in solution .....	0.009
Total.....	0.040

This total represents sulphur occurring in difficultly volatile organic compounds and does not include that which is evolved in more volatile compounds. It is not impossible that a loss by

volatization occurred in evaporating the chloroform extracts preparatory to combustion in nitrous oxide. It seemed very desirable to learn more of the nature of these organic sulphur compounds and accordingly the following experiment was tried with a larger quantity of iron.

*Experiment 6.* One thousand grams of the same white iron as had been used in the preceding experiments were treated in small portions at a time with hydrochloric acid of 1.15 sp. gr. until the solution was complete. To hasten the process, as the action of the acid became slow, the flask was gently warmed. The escaping gas was passed, first, through a solution of lead acetate supersaturated with sodium hydroxide, and secondly, through a solution of mercuric chloride in alcohol.

#### I. THE ALKALINE LEAD ACETATE SOLUTION.

In addition to the deposit of lead sulphide which formed in the lead solution, a yellow flocculent precipitate appeared, soluble on shaking in the alkaline fluid. The solution, decanted from the lead sulphide, was slightly acidulated and warmed. The gas produced was found to yield the following reactions with the solutions named:

Ammoniacal cadmium chloride yielded a white flocculent precipitate.

Palladium chloride yielded a cinnamon colored precipitate.

Platinum chloride yielded a yellowish brown precipitate.

Ammoniacal silver nitrate yielded a pale yellow precipitate.

These reactions indicated the presence of a mercaptan. To study the subject more fully the yellow precipitate, produced in a solution of silver nitrate containing an excess of sodium acetate, was subjected to a partial analysis with the following results:

Silver.	Found.	Sulphur.	Silver.	Sulphur.
			Calculated for silver mercaptide.	
69.40		20.54	69.63	20.68

From the data so obtained it appears that methyl hydrosulphide was contained in the gas evolved during the solution of the iron in the hydrochloric acid.

#### 2. THE ALCOHOLIC SOLUTION OF MERCURIC CHLORIDE.

This was found to contain a small quantity of a white precipi-

tate which was partly soluble on warming. After cooling again the solution yielded transparent colorless crystals recognized under the microscope as having the form of crystals of the compound  $(\text{CH}_3)_2\text{SHgCl}$ , which results when methyl sulphide is added to a solution of mercuric chloride. Upon boiling the aqueous solution of the precipitate in the mercuric chloride solution and leading the vapors into palladium chloride solution, orange crystals were obtained which under the microscope were not distinguishable from the compound formed when palladium chloride and methyl sulphide are brought together. The precipitates formed in the solutions of mercuric chloride and palladium chloride being somewhat soluble, the quantity obtained was insufficient for analysis. It is however very probable that methyl sulphide  $(\text{CH}_3)_2\text{S}$  occurred among the gases evolved during the solution of the iron.

It seems important that in the evolution method of sulphur determination the possibility of the presence of these and kindred sulphur compounds should be taken into account. Two modes of procedure suggest themselves for the recovery of that portion of the sulphur which is liable to be lost in the determination.

I. By direct oxidation to sulphuric acid.

II. By conversion into hydrogen sulphide followed by oxidation to sulphuric acid.

#### I. DIRECT OXIDATION OF ORGANIC SULPHUR COMPOUNDS.

The action of concentrated nitric acid, potassium permanganate and other energetic oxidizing agents in solution tends merely to convert methyl sulphide into its oxides  $(\text{CH}_3)_2\text{SO}$  and  $(\text{CH}_3)_2\text{SO}_2$ . Bromine enters into direct union forming  $(\text{CH}_3)_2\text{SBr}_2$ .

Under strongly oxidizing influences methyl hydrosulphide merely yields methylsulphonic acid, an acid which is well known to form a soluble and stable barium salt. Hence while it is a characteristic property of hydrogen sulphide to undergo oxidation to sulphuric acid readily, it is equally characteristic of these organic sulphur compounds and their homologues not to change easily into sulphuric acid even under apparently favorable conditions.

It seemed possible that by direct combustion of the gases the complete oxidation of the sulphur to sulphuric acid might be effected.

A great many experiments have been tried in this direction of which the following is a summary.

As the gases are not evolved in sufficient quantity during the solution of the iron to burn steadily from a jet, it was found necessary to conduct through the evolution flask a current of some combustible gas in order to maintain a more constant flame. For this purpose carbon monoxide was used. The gas was burned from a platinum jet in a glass globe through which a current of moist nitrous oxide was caused to flow. Nitrous oxide was used rather than air or oxygen for the reason that during the combustion of any gas in it nitrogen dioxide is continually formed in considerable quantity. The conditions are therefore highly favorable to the oxidation of any sulphur dioxide produced from the flame of the burning gas, and the complete condensation of the resulting sulphuric acid.

The results were not satisfactory for two reasons :

1. It was found impossible to prevent the occasional extinguishing of the flame, due to the slight pulsations in the gas stream.
2. It was not possible to expel all of the less volatile hydrocarbon oils from the evolution flask into the combustion globe without boiling the ferrous chloride solution and consequent risk of driving over too much steam which tended to extinguish the flame. These difficulties necessitated the abandonment of the method.

## II. CONVERSION OF ORGANIC SULPHUR COMPOUNDS INTO HYDROGEN SULPHIDE.

The precipitates produced by the mercaptans in solutions of metallic salts, are not easily converted into sulphides. From this statement must be partially excepted the lead, silver and copper compounds which may change slowly into sulphides. The cadmium compound, which is often seen as a white precipitate when in the evolution method ammoniacal cadmium chloride is used as an absorbent, is more stable. The white precipitate gradually changes into yellow cadmium sulphide, especially on exposure to light.



The process adopted by Blair—absorption in alkaline lead solution—no doubt possesses an advantage on account of the possible change of the lead compound into lead sulphide, as it in this way may affect the recovery of a portion of the lost sulphur. The compounds of the sulphur ethers of the type  $\text{HgCl}_2(\text{CH}_3)_2\text{S}$  are still less prone to change into metallic sulphides under the conditions imposed by the method.

*Experiment 7.*—The vapor of methyl sulphide largely diluted with carbon dioxide was passed through a red hot porcelain tube. By this treatment the sulphur compound was shown to be readily convertible into hydrogen sulphide, undergoing, however, an intermediate transformation into methyl hydrosulphide,  $\text{CH}_3\text{SH}$ , a gas which is easily recognized by its reactions with various metallic salts in solution.

Based upon the results of these experiments the following modification of the evolution method was tried:

The iron was dissolved in hydrochloric acid of 1.12 sp. gr. added slowly while a stream of carbon dioxide was being transmitted through the flask. Heat was applied as soon as the action became retarded. The escaping gas was led through a porcelain combustion tube heated to dull redness. The porcelain tube contained a roll of platinum foil eight inches long. The delivery tube from the evolution flask was pushed far enough into the porcelain tube to permit any liquid which might distil over to drop into the hot platinum roll. A slow stream of carbon dioxide was passed continuously through the evolution flask and heated porcelain tube. The solution of the ferrous chloride was finally heated to gentle boiling and kept boiling until the oily drops which usually coat the sides of the flask were carried away. This required two hour's boiling or two and one-half hours for the entire process. Inasmuch as organic compounds of high boiling-point are undoubtedly formed, this long-continued boiling is especially important. As an absorbent, bromine dissolved in dilute hydrochloric acid was used. After passing a nitrogen flask containing the bromine solution the gas was conducted to the bottom of an eight liter bottle containing a little of the same bromine solution. Experiments have shown that the use of this large bottle is necessary to the complete con-

densation of the sulphuric acid. The platinum foil used in the porcelain tube is not essential but protects the porcelain tube from risk of fracture from the dropping of the liquid upon its heated inner surface. Mica may be used instead of platinum but is rapidly corroded by the hot acid vapors. The sulphur was determined by weighing as barium sulphate.

In the following table column II contains the results of some determinations of sulphur by the method described.

Column I contains results obtained by the same method except that no heated tube was used.

Column III contains results obtained by the aqua regia method as described by Blair.<sup>1</sup>

The irons used for the determinations were selected on account of their high percentage of sulphur.

Evolution method. Per cent.	Evolution method. Gases passed through a heated tube. Per cent.	Aqua regia method of Blair. Per cent.
IRON A.		
0.059	0.096	0.101
0.046	0.095	0.098
0.050	0.104	0.096
0.050	0.104	0.099
0.054	0.099	0.100
0.055	0.100	0.102
....	0.092	0.102
....	0.105	0.104
....	0.098	....
....	0.101	....
Mean 0.052	0.099	0.100
IRON B.		
0.100	0.183	0.173
0.101	0.178	0.170
0.087	0.175	0.168
0.099	0.181	0.170
0.092	0.177	0.174
0.084	0.188	0.171
Mean 0.094	0.180	0.171

In conclusion, I have to thank Messrs. F. B. Smith and H. C. Beggs for the very great care they have taken in carrying out the determinations by the method described.

<sup>1</sup> Chemical Analysis of Iron, p. 57.

## ON THE VOLUMETRIC DETERMINATION OF LEAD.

BY ALLERTON S. CUSHMAN AND J. HAYES-CAMPBELL.

Received September 26, 1895.

FRESENIUS in the last edition of his *Quantitative Analysis* commenting on the volumetric determination of lead, says : " Although there is no lack of proposed methods for the volumetric estimation of lead, we are still without a really good method for practical purposes, that is, a method which can be generally employed, and which is simple and exact."

Among the methods which have been proposed, one which has been so much used is that of Schwartz,<sup>1</sup> briefly outlined. This depends upon precipitating the lead as chromate in a sodium acetate solution with a standard solution of potassium bichromate, the end point being determined by an outside indicator consisting of drops of a neutral solution of silver nitrate on a porcelain plate. It is exceedingly difficult to decide when the first red tinge makes its appearance in the indicator owing to the yellow color of the precipitated lead chromate. The end point is therefore frequently overrun. W. Diehle<sup>2</sup> modified the method by titrating the excess of bichromate in acid solution with sodium thiosulphate, the end point being indicated by the disappearance of the yellow color of the bichromate. In our experience this modification does not lessen the difficulty of determining accurately the end point, owing to the fact that the yellow color gradually shades off into a green in case a fair excess of bichromate has been added.

These considerations led us to endeavor to modify the original method in such a manner as to secure a simple and accurate means of determining the excess of bichromate present. This we accomplish by titrating the solution after filtering off the precipitated lead chromate, with a standardized solution of ammonio ferrous sulphate, using potassium ferricyanide as an outside indicator under exactly the same conditions observed in standardizing bichromate solutions. The bichromate solution is made up of convenient empirical strength, and standardized against a weighed amount of pure dried ammonio ferrous sulphate. Slightly more than the equivalent weight of the latter salt is then

<sup>1</sup> *Dingl. poly. Jour.*, 169, 284.

<sup>2</sup> *Ztschr. anal. Chem.*, 1880, 306.

weighed out and dissolved in a liter of water with the addition of a few drops of sulphuric acid. The solution is transferred to a stock bottle into which is immediately poured a sufficient quantity of some light paraffin oil to form a layer over the solution, thus protecting it from oxidation. The stock bottle is fitted with a siphon tube and pinchcock so that the solution can be drawn out when needed. With this arrangement change in strength of the ammonio ferrous sulphate solution takes place very slowly, while as a few moments only are required to titrate it against the standard bichromate, its exact strength can be easily determined from day to day.

In order to test this modification, we decided to try it against other technical methods recently proposed, as well as against a standard gravimetric analysis. A well mixed sample of a crystallized galena containing only a little silica as impurity was first analyzed by the method of Rose as given in Fresenius, Quantitative Analysis. The lead is precipitated as the sulphide, with the proper precautions, the sulphide is then dried, ignited gently in a current of hydrogen, and weighed. The following results were obtained :

No.	Weight taken. Grams.	Weight lead sulphide. Grams.	Lead sulphide. Per cent.	Lead. Per cent.
1	2.0000	1.9870	99.35	86.08
2	2.0000	1.9856	99.28	86.00
3	1.9988	1.9856	99.35	86.06

The next series of results were obtained by the method of Albert H. Low.<sup>1</sup> Briefly, the method consists in decomposing the ore with nitric and sulphuric acids, adding further an excess of sulphuric acid, dissolving the lead sulphate in a saturated solution of ammonium chloride and precipitating metallic lead by means of strips of aluminum. The precipitated lead sponge is scraped off, pressed into a button, dried and weighed. By this method the following results were obtained :

No.	Weight taken. Grams.	Weight lead. Grams.	Lead. Per cent.
1	0.5000	0.4341	86.82
2	0.5013	0.4311	86.00
3	0.4972	0.4313	86.64
4	0.5025	0.4371	86.98
5	0.5019	0.4351	86.25
6	0.5223	0.4540	86.92

<sup>1</sup> *J. Anal. Appl. Chem.*, 6, 12.

These figures show a general tendency to high results which is accounted for by the difficulty of washing the lead sponge free from ammonium chloride. In view of the fact, however, that one of these assays can be made in about twenty-five minutes, the results might be considered fair enough for some technical purposes.

The next method tried was Knight's<sup>1</sup> modification of Hempel's method. This consists essentially in the precipitation of the lead as oxalate, the decomposition of this salt by means of sulphuric acid and titration of the liberated oxalic acid, with potassium permanganate. This method did not yield concordant results in our hands and the percentages found were invariably low. As the method did not present any advantage over others either in points of accuracy or time, we discontinued work with it.

The modified Schwartz method we carry out as follows: About one gram of finely pulverized ore is digested in a casserole or evaporating dish with fifteen cc. of a mixture of two parts nitric and one part sulphuric acid until decomposition is complete. Ten cc. more of sulphuric acid are now added, and the liquid evaporated until it fumes freely. Cool, dilute with ten cc. of dilute sulphuric acid (1-10) and then add gradually forty cc. of water. Heat to boiling, filter and wash by decantation with dilute sulphuric acid (1-10) getting as little of the lead sulphate on the filter as possible. To the residue in the dish add twenty cc. of strong ammonia, then make slightly acid with acetic acid. Boil until the lead sulphate is dissolved, then pour the liquid through the filter, having first moistened the paper with ammonia. Wash the filter with water containing ammonium acetate in solution, and finally once or twice with hot water. Cool the filtrate and run in from a burette an excess of standard bichromate solution, stirring until the precipitate settles rapidly and the supernatant liquid has a yellow color. Allow to settle for a few minutes then filter, under pressure if possible, wash a few times and titrate the filtrate against the standard ammonio ferrous sulphate.

After a little practice the method can be carried out as above detailed in about thirty minutes. In case the ore is known to be

<sup>1</sup> *J. Anal. Appl. Chem.*, 6, 11.

free from bismuth and antimony, the method can be materially shortened. Instead of bringing the ore into solution with a mixture of nitric and sulphuric acids, nitric acid alone is used. After solution, the acid is neutralized with an excess of ammonia and then made acid with acetic acid; this dissolves any lead sulphate that has been formed. This solution is then immediately titrated with the bichromate and ammonio ferrous sulphate solutions exactly as described above. The following table shows the agreement in the results obtained by this method:

No.	Weight taken. Grams.	Calculated weight lead found. Grams.	Lead per cent.
1	0.9983	0.8570	85.84
2	0.9987	0.8578	85.82
3	0.9997	0.8588	86.08
4	0.9806	0.8421	85.88
5	0.9996	0.8570	85.72
6	0.9971	0.8558	85.84
7	0.9975	0.8580	86.02
8	0.9936	0.8533	85.90

In general it may be said that the results are a trifle low. The mean of the amount of lead recovered in twenty determinations carried out by one of us was 99.6 per cent. of that taken.

We do not know that the modification as used by us has never before been tried, but our results appeared to possess sufficient value to warrant publication.

CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY,  
ST. LOUIS, MO.

## REACTIONS BETWEEN COPPER AND CONCENTRATED SULPHURIC ACID.<sup>1</sup>

BY CHAS. BASKERVILLE.

Received September 9, 1895.

ANDREWS<sup>2</sup> in writing on the "Assumption of a Special Nascent State," argued that the production of sulphur dioxide, as a result of the reaction between copper and concentrated sulphuric acid, was due not to nascent hydrogen, as is commonly considered, but to the deoxidation of sulphur trioxide by the copper with the production of copper oxide as a primary pro-

<sup>1</sup> Read at the Springfield meeting.

<sup>2</sup> Chem. News, 70, 152; Iowa Acad. of Sciences, Proc. p. 4.

duct. Having noted frequently the evolution of sulphur dioxide gas before any evidence of this "copper oxide," at the suggestion of Dr. F. P. Venable, I began some experiments with a view of studying this complicated reaction so simply treated in most text-books.

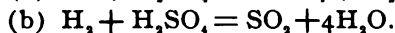
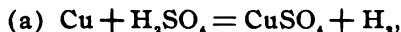
When my work was completed, in verifying my references I chanced on Pickering's<sup>1</sup> work on the same subject, which had escaped me. Most of my work, especially that part which concerns the secondary reactions, is in accord with that of Prof. Pickering. My observations concerning the primary reactions were not the same however. In making known the latter, I feel at liberty to give the results of my work, as independent corroboration is of some value.

The reactions which take place when copper is treated with concentrated sulphuric acid may be divided into primary and secondary.

Primary:



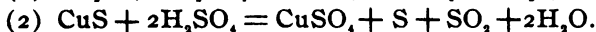
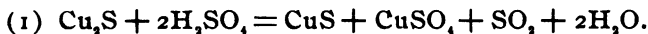
This may be regarded as taking place in two steps:



Still no hydrogen could be detected in the gas given off.



Secondary:



The experiments were carried out under various conditions of temperature and time, exposure of the metal to the action of the acid, and varying proportions of metal and acid. The copper ribbon used was cut into small pieces one cm. wide by two to three cm. long. Concentrated C. P. sulphuric acid, 1.84 sp. gr. was used. Each experiment, except where noted, was carried out in a flask in which the air had been displaced by a neutral gas, hydrogen or carbon dioxide. The evolved sulphur dioxide was led through a strong solution of sodium hydroxide

<sup>1</sup> J. Lond. Chem. Soc. Trans., 1878, p. 112.

and the sulphite formed titrated with a standard iodine solution or oxidized by bromine, and the sulphuric acid determined gravimetrically. A rapid stream of the inert gas was driven through the apparatus just at the close of the experiment. Water was poured into the flask and the whole quickly filtered, and the copper remaining unattacked was then cleaned as well as possible by rubbing, dried and weighed. The copper as sulphate was determined by electrolysis. The residue was burned in a porcelain crucible, treated with concentrated nitric acid, ignited and weighed as copper oxide. Sulphur was determined by weighing a dried portion of the residue treating with carbon disulphide and the loss in weight taken as sulphur.

*Primary Reactions.*—My experiments showed that the first of the primary reactions predominated when copper was treated with concentrated sulphuric acid at different temperatures ( $0^{\circ}$ – $270^{\circ}$  C.) At the highest temperature it was found that that reaction alone took place, but at all lower temperatures the second primary reaction also occurred. The proportion of the material following the second equation increased from  $0^{\circ}$  to  $100^{\circ}$  C., and then decreased to  $270^{\circ}$  C., when there was no longer evidence of any such reaction, that is, no black residue was formed.

At the lower temperatures, under  $100^{\circ}$  C., only the two primary reactions seemed to take place; at the higher temperatures the secondary reactions if the action were prolonged, frequently set in, complicating matters as far as quantitative determinations were concerned. If the time of action were shortened evidence of the occurrence of the primary reactions alone was found. Having an excess of copper present was also necessary, because as soon as all the copper had been attacked the secondary reactions set in at once.

The conditions seemed most favorable for the formation of the insoluble residue at the temperatures from  $100^{\circ}$  to  $130^{\circ}$  C. as may be seen from the table. The proportion of the insoluble residue decreases rapidly in either direction from these temperatures. Some insoluble residue is produced at all the lower temperatures but none is produced when the reaction takes place at  $270^{\circ}$  C. and lasts for only a few seconds.



No.	Temperature of reaction.	Copper used.	Copper sulphate.	Copper as sulphide.	Sulphur dioxide produced.	Ratio of copper sulphate to copper sulphide.
1	0°-10°	0.1350	0.1340	0.0005	0.1343	268.0 : 1
2	"	0.0750	0.0740	0.0003	0.0780	246.0 : 1
3	20°-30°	1.3379	1.3260	0.0121	....	118.9 : 1
4	"	1.2473	1.2000	0.0184	1.2442	68.0 : 1
5	65°	0.1650	0.1600	0.0050	0.1648	33.0 : 1
6	70°-80°	0.0760	0.0730	0.0035	....	21.0 : 1
7	100°	0.1380	0.1060	0.0300	0.0840	3.5 : 2
8	"	0.3818	0.2800	0.1082	0.1166	3.5 : 1
9	"	0.9200	0.6400	0.2748	0.2165	3.3 : 1
10	120°-130°	5.2578	4.0800	1.1946	2.0932	3.5 : 1
11	140°-160°	5.0900	4.5100	0.5759	3.3084	8.0 : 1
12	160°-190°	1.1375	1.1200	0.0930	....	12.0 : 1
13	200°-220°	1.5450	1.4518	0.0932	1.0904	16.0 : 1
14	220°-230°	0.9815	0.9400	0.0332	0.9365	29.0 : 1
15	230°	3.8915	3.8200	0.0796	3.6327	49.0 : 1
16	230°	2.0000	1.9750	0.0388	2.2313	51.0 : 1
17	240°	1.1235	1.1035	0.0200	0.9855	55.0 : 1
18	250°-260°	2.1365	2.1000	0.0280	2.0304	80.0 : 1
19	270°	4.0000	....	None.	....	....

Berzelius<sup>1</sup> noted this black substance when copper was treated with concentrated sulphuric acid. He said it appeared to be a subsulphate because it was oxidizable by nitric acid. He made no quantitative determinations to show its composition. Such a body would contain fifty-seven per cent. of copper and in no case did I find the black residue to contain less than 67.64 per cent.

Barruel<sup>2</sup> found that sulphuric acid acted on copper at ordinary temperatures if sufficient time were given. He claimed that the sulphur dioxide produced was dissolved in the acid and attacked the copper forming copper sulphide and oxide, the latter being dissolved in the acid.

Maumené<sup>3</sup> claimed that his black residue contained four different bodies; copper subsulphide and three oxysulphides,  $\text{CuO} \cdot 2\text{Cu}_2\text{S}$  or  $\text{Cu}_4\text{S}_2\text{O}_7$ ,  $\text{CuO} \cdot 2\text{CuS}$  or  $\text{Cu}_3\text{S}_2\text{O}_7$ , and  $\text{CuO} \cdot \text{CuS}$  or  $\text{Cu}_2\text{SO}$ .

In my analyses, as also in Pickering's, the sum of the percent-

<sup>1</sup> *Traité de chimie*, 4, 324.

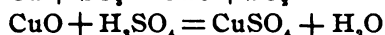
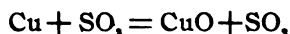
<sup>2</sup> *Journ. de Pharm.* 20, 13, 1834.

<sup>3</sup> *Ann. Chim. Phys.*, 1846, 3rd Series, 18, 311; *Traité de chimie générale*, Pelouze et Fremy, 2nd Ed., I. 388.

ages of copper and sulphur always approximated 100. In one experiment I did find a body whose composition approximated  $\text{CuO}_2\text{Cu}_4\text{S}$ . I shall speak of that apparent exception further on.

Calvert and Johnson<sup>1</sup> performed some experiments on the action of strong and dilute sulphuric acid on copper at temperatures from  $130^\circ$  to  $150^\circ$  C. They noted the formation of the sub-sulphide and claimed it was due to the liberation of free sulphur which afterwards combined with the copper direct.<sup>2</sup> There was evidently something very wrong in their observations, for they failed to note any action below  $130^\circ$  C. Barruel in 1834 had noted that action took place at the temperature of the air. I have noted the action at  $0^\circ$  C.

According to Andrews



are the correct formulas,  $\text{SO}_2$  existing at the temperature necessary for the reaction, and the insoluble residue being the oxide. That would do if the reaction occurred only at those higher temperatures, whereas it occurs as well at  $0^\circ$  C. Besides this the undissolved residue is not the oxide at all, as he says it is, but invariably the sulphide. In making his analyses very likely he determined the copper alone and the percentage of copper in copper oxide and cuprous sulphide is the same. In a subsequent conversation with Dr. Andrews, I have learned that this was the case. This black residue when thoroughly washed free from any sulphuric acid always gave off hydrogen sulphide on treatment with hydrochloric acid.

The composition of the insoluble residue was determined by analysis:

	Found.		Calculated for $\text{Cu}_2\text{S}$ .
Sulphur.....	20.44		20.14
Copper.....	79.56	(by difference)	79.86
	<u>100.00</u>		<u>100.00</u>

In the first of the two primary reactions,



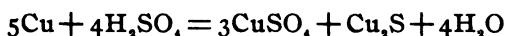
<sup>1</sup> J. Chem. Soc., 19, 438, 1866.

<sup>2</sup> Pickering proved this impossible. The amount of sulphide produced was not increased by adding sulphur direct to the experiment.

it is seen that for each atom of copper found as sulphate, one molecule of sulphur dioxide should be evolved. Calculating on this basis from the following table we have the ratio of 2 : 3 between the copper as subsulphide and the copper as sulphate unaccounted for in the production of the sulphur dioxide.

No.	Sulphur dioxide.	Corresponding copper.	Total copper as sulphate.	Copper as sulphide.	Difference. Columns 3 and 4.	Ratio. Columns 5 and 6.
8	0.1166	0.1158	0.2800	0.1082	0.1642	2 : 3
9	0.2165	0.2132	0.6400	0.2758	0.4268	2 : 3

The formula



shows that relation between the two compounds of copper.<sup>1</sup>

*Secondary Reactions.*—The secondary reactions depend upon the second of the primary, that is, the cuprous sulphide produced. If the experiment were carried out so as to cause a rapid evolution of gas and the residue not allowed to form a protective coating over the copper, as long as an excess of the metal was present, only the primary reactions occurred. This was accomplished at 160°–170° C. If the strips of copper were touching they almost always became bound together by the anhydrous copper sulphate and a coating of the black residue formed a protective covering to the copper. When such a state of affairs occurred, no sharply defined line could be drawn to show, of these secondary reactions, when the first ends and the second begins, because as soon as some cuprous sulphide is changed to cupric sulphide, the latter is attacked by the sulphuric acid, sulphur being one of the products of the last reaction. Several experiments carried out at 140°–150° C when this occurred with an excess of copper gave evidence of all the reactions, primary and secondary. Sulphur was deposited on the sides of the flask and the black residue contained 20.71 per cent. sulphur, and the theoretical percentage for cuprous sulphide is 20.138. This showed the presence of some cupric sulphide in which the percentage of sulphur is 33.59.<sup>2</sup>

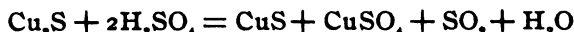
<sup>1</sup> Pickering states (*loc. cit.*, p 117) that once at 80° C. he observed that the copper in the two compounds stood in the relation of 2 : 2.9. I have not been able, however, to have concentrated sulphuric acid act on copper at any temperature from 0° C. to 270° C. without the evolution of sulphur dioxide, which is not accounted for at all in case the second of the primary reactions alone takes place, which he states did take place at 80° C.

<sup>2</sup> Watts (vol. II, p. 41, 1875, Ed.) notes this complete decomposition.

Some freshly prepared cuprous sulphide was treated with concentrated sulphuric acid. Sulphur was determined in the undissolved residue, the free sulphur being first removed.

	Found.	Calculated for CuS.
Sulphur .....	32.36	33.59

The formula,



explains such a change.

Another portion of cuprous sulphide was boiled with concentrated acid until it nearly all disappeared. The free sulphur produced was determined.

	Found.	Calculated.
Sulphur .....	19.71	20.138

The formula



shows the final result of the continued action of sulphuric acid on the subsulphide.

From these data the secondary reactions between copper and concentrated sulphuric acid may be expressed by the two formulas,

1.  $\text{Cu}_2\text{S} + 2\text{H}_2\text{SO}_4 = \text{CuS} + \text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}.$
2.  $\text{CuS} + 2\text{H}_2\text{SO}_4 = \text{S} + \text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}.$

The occurrence of sulphur on the sides of the flask at the end of the reaction may be said to be due to the sublimation of that element which is produced by the direct decomposition of sulphuric acid without the intermediate formation of hydrogen sulphide for the following reasons :

1. If hydrogen sulphide were produced by the decomposition of the sulphide, it is natural to expect some to escape in the gases which are given off. None could be detected.
2. As is well known, hydrogen sulphide is decomposed by concentrated sulphuric acid.
3. The deposit of sulphur is first noted on the sides of the flask and not in the delivery tube where the gases, hydrogen sulphide, and sulphur dioxide, would naturally come into the most intimate relations.
4. If flowers of sulphur be heated with concentrated sulphuric

acid in a flask provided with a long outlet tube, much of the sulphur will be seen to creep up the sides of the flask, and some sublimed even into the tube, which shows that the state of affairs observed may be attained without any trace of hydrogen sulphide being present.

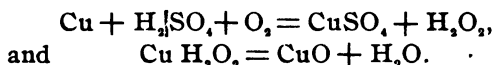
#### COPPER OXYSULPHIDE.

Contradictory evidence to what has been stated above was found in one case where the insoluble residue approximated  $\text{CuO} \cdot 2\text{Cu}_2\text{S}$  in composition. This is one of the oxysulphides stated by Maumené to exist in the black residue. The acid was heated to  $250^\circ \text{C}$ . in an Erlenmeyer flask. The air was not removed by an inert gas. The copper was suspended in long strips, only a third of which was immersed in the acid, the other part being exposed to the air.

The black residue formed under these conditions gave on analysis :

	Found.	Calculated for $\text{CuO} \cdot 2\text{Cu}_2\text{S}$ .
Sulphur .....	16.16	16.15
Oxygen .....	3.54	4.03
Copper .....	undetermined	79.82

Schuster<sup>1</sup> found that copper was acted on by dilute sulphuric acid only in the presence of atmospheric oxygen. Traube<sup>2</sup> noted that copper was not oxidized in moist air, but was slowly in the presence of dilute sulphuric acid. Although copper is unable to decompose sulphuric acid at ordinary temperatures (according to Traube) its affinity for  $\text{SO}_4$  and that of hydrogen for oxygen are together sufficient to cause such a decomposition, the probable reaction being :



I could detect no oxygen in the gases given off when the experiments were carried out in an inert atmosphere. Nor could I detect hydrogen peroxide. Traube himself states that no "active" oxygen was liberated in the reaction because carbon monoxide was not oxidized to carbon dioxide. Pickering<sup>3</sup> sug-

<sup>1</sup> Proc. Roy. Soc., 55, 84; Ber. d. chem. Ges., 28, 219.

<sup>2</sup> Ber. d. chem. Ges., 18, 1887-1890.

<sup>3</sup> Loc. cit., p. 138.

gests that the sulphide formed is "oxidized at the time of its appearance by the oxygen which would be liberated at the surface of that portion of the copper which is immersed in the acid, since the whole arrangement would form a galvanic cell consisting of a metal, a liquid, and a gas."

UNIVERSITY OF NORTH CAROLINA.

---

### NEW BOOKS.

PRINCIPLES AND PRACTICE OF AGRICULTURAL ANALYSIS. BY HARVEY W. WILEY. Volume 1, Soils. Cloth, 8 vo., pp. 607, figures, 93. Easton: Chemical Publishing Co. 1894. Price, \$3.75.

This first bound volume includes the first eight parts of the compendious work now in process of publication.

In attempting to meet the wants alike of analysts, teachers, and students of agricultural chemistry, the author has undertaken a most difficult task. The needs of the several classes of readers are widely different, often distinctly opposite.

Beyond doubt, each of the classes named has need of a thoroughly modern treatise upon this subject. There is extant no satisfactory systematic introduction through the general principles of analysis to the special methods applicable to agricultural materials; the student is ordinarily compelled to the study of many methods, in the illustration of general principles and for the acquirement of facility in manipulation, that are not directly required in his future work, and which might often be happily substituted by methods which are of immediate use. Again, there is no English work on agricultural analysis—except of the most incomplete scope—which is at all modern; nor does any work upon the subject in any language cover the methods developed in America during the past ten years. On the other side, the Proceedings of the Association of Official Agricultural Chemists state the American official methods most briefly, for the guidance of analysts presumably acquainted with the methods in general, and more or less familiar with the reasons for the several specifications; and, therefore, without explanatory comment; nor has this Association undertaken, as yet, to cover all of the large field involved. Even assuming a degree of linguistic attainment altogether beyond that of the average student, and of

many a practicing analyst, the foreign treatises upon the subject are often so brief as to mislead the student and to be useless even to the practicing analyst. The opening for a treatise of the design outlined by Professor Wiley is therefore wide.

The perspective of the volume will serve quite well, perhaps, to elucidate the author's treatment of his subject in its salient features; of 607 pages, over one-tenth is devoted to a brief study of the materials to be analyzed, and their origin; one-twentieth is given to the sampling of the soil; one-seventh to the physical properties of the soil, including their estimation; one-sixth to mechanical and mineralogical analysis; one-thirtieth to the determination of the gases of the soil; the remaining half of the volume deals with the chemical analysis of the soil, including soil waters.

In no other treatise of this kind are the relations of the analytical method to the nature of the problem it is used to solve, so fully dwelt upon; and in no other similar treatise do the physical and mineralogical properties receive a treatment so fully in accord with their importance.

The style is clear and compact. In his selection of methods no attempt has been made by the author to limit those described to the number found useful in a single laboratory only, but general experience has rather been consulted. Especial stress is laid upon American methods because the reader will chiefly use these methods, and because other treatises so frequently ignore them; yet no other treatise gives nearly as full discussion even to the Continental official methods, and the judicial impartiality of the author is highly praiseworthy. The very recent literature has been drawn upon for material, and the wealth of reference will be especially appreciated by the teacher and analyst; this volume alone contains 348 listed references to original papers.

This work is furthermore noteworthy as being probably the first important chemical treatise to rigidly follow the American Association for the Advancement of Science revision of chemical orthography. The practice of beginning with a lower-case type all proper names used in the text to designate methods is an innovation less certain to be followed. The figures are well selected and apposite.

The publishers are to be congratulated on the beautiful typography of the volume, its good press-work, and its freedom from printer's errors.

Judging of this work by the first volume it may be said, briefly, that it is the most modern, the most complete and the very best treatise upon the subject of agricultural analysis, and that it meets more largely than any other book on the subject, the needs of the teacher, the student, and the working analyst. It is not, of course, a text-book of agricultural chemical analysis, nor a hand-book of the laboratory, but it should find its place upon the reference tables of all laboratories. Nor is its usefulness confined to the analyst of agricultural products alone, for every general analyst will find in its pages a great mass of material, superbly arranged, to which he could daily refer with direct advantage to his work.

WILLIAM FREAR.

A HAND-BOOK OF INDUSTRIAL ORGANIC CHEMISTRY. BY SAMUEL P. SADTLER, PH.D., F.C.S. Second revised and enlarged edition. 8 vo. pp. 537. Philadelphia: J. B. Lippincott & Co. 1895. Price, cloth \$5.00, sheep \$6.00.

The hundreds of manufacturers of chemical products in this and other countries who are struggling with the puzzling problems of daily practice and the vexatious details so essential to commercial success, eagerly watch for and greedily accept everything which may possibly clear up difficulties or offer suggestions, and such works as this of Dr. Sadtler's find the heartiest of welcomes waiting for them. It is not surprising, therefore, that this work from so excellent authority should soon be out of print and that a second edition should be needed to meet the current demand.

Limited in volume, and, therefore, in detail, works of this class serve two important purposes: First, they furnish teachers in compact and reliable form for presentation to their students, ample description of the principles and processes used in the chemical industries. Second, they furnish manufacturers, working in more or less empirical ways, knowledge of the fundamental principles of the processes they employ, or general principles of methods other than their own but attaining the same end, possibly with greater economy both of time and means.

In the second instance they meet only partially the prevailing



demand. Manufacturers are desirous, it is true, of becoming acquainted with the experience of others even in other branches of industry, but the difficulties they meet are frequently, if not generally, as much mechanical as chemical, and better and more effective forms of apparatus as well as general reactions are needed. Furthermore, profits in manufacture depend in these days largely upon the utilization of the waste products, and the practical operation of many processes are dependent upon the retention or destruction of wastes, noxious or undesirable. Methods and apparatus are wanted for properly caring for these important factors of the industrial problems.

In the work before us Dr. Sadtler has succinctly set forth the progress attained to date in the industries discussed and in a large measure has met the demands described. Perfection is rare, and doubtless many of us might be able to suggest additions to the several chapters dictated by personal experience; yet with the material offered, together with the bibliography, the references to other and larger works and particularly to the periodical literature, it is questionable if one can find a better time saver in all the range of technical-chemical publications than is provided in this work.

In fourteen chapters, covering 492 pages, the industries most common to this country, at least, are discussed under five general heads, *viz*: Raw materials; Processes of manufacture; Products; Analytical tests and methods; Bibliography and statistics; and in this systematic way the essential facts are presented. Descriptions for empirical work are accompanied by analytical methods for rational control. In addition thereto is an appendix giving conversion tables and tables of physical and chemical constants useful wherever the work may go.

One hundred and twenty-seven most excellent cuts representing machinery and apparatus used in the works or laboratories illustrate the text and fourteen diagrams illustrate the various successive steps in processes of manufacture or analysis. A thoroughly complete index makes reference most convenient and will charm those who have suffered the vexation incident to the use of books not similarly provided.

WILLIAM MCMURTRIE.

## BOOKS RECEIVED:

On the Densities of Oxygen and Hydrogen, and on the Ratio of their Atomic Weights. By Edward W. Morley, Ph.D. City of Washington, published by the Smithsonian Institution, 1895. 4° xi, 117 pp. Price \$1.00.

*From Smithsonian Contributions to Knowledge, Vol. XXIX. (Number 980.)*

The Scientific Foundations of Analytical Chemistry. By Wilhelm Ostwald, Ph.D. Translated by George M'Gowan, Ph.D. New York, published by Macmillan & Co., 1895. 8°. xviii, 207 pp. Price \$1.60.

Organic Chemistry. The Fatty Compounds. By R. Lloyd Whiteley, F.I.C., F.C.S. New York, published by Longmans, Green & Co., 1895. 8°. viii, 291 pp. Price \$1.00.

A Manual of Qualitative Chemical Analysis. By E. P. Harris, Ph.D., LL.D. New edition, revised. Amherst, Mass., printed by Carpenter & Morehouse. 8°. 315 pp. Price \$1.50.

Maps of British Columbia, Nova Scotia, Quebec and Ontario. Ottawa, the Geological Survey of Canada. 1895.

Practical Proofs of Chemical Laws. By Vaughan Cornish, M. Sc. London and New York, published by Longmans, Green & Co., 1895. xii, 92 pp. Price 75 cents.

# THE JOURNAL

OF THE

# AMERICAN CHEMICAL SOCIETY.

---

## A CONVENIENT STILL FOR THE LABORATORY.<sup>1</sup>

BY CHARLES E. WAIT.

Received October 14, 1895.

**I**N the use of the apparatus purchased for the new chemical laboratories of the university, no piece has given us more satisfaction, or has been a greater success, than a new still, which is the subject of this paper. In the designing of this still I had two definite objects in view; one, the utilizing of steam from the large sixty horse-power boiler used in heating the building, and the other, a provision for making distilled water with gas, when steam from the heating-plant was not available. The still is encased in wrought-iron, with a lining of asbestos, and is provided with a float which automatically regulates the flow of water from the supply-pipe. It is a beautiful piece of apparatus, and the workmanship is excellent in every detail. The essential parts of this apparatus will be understood by consulting the accompanying figures, but a few words of explanation may be appropriate. The still has a capacity of seven gallons, and is made of heavy copper, tin-lined. It has a water-gauge showing the height of the water in the still, also an exit for steam, and safety-valve, V; inlet for steam through a coiled perforated block-tin pipe; also an outlet, O, for cleaning out the still; and there is also a heavy disk gas-burner. There is a conveniently-arranged drying-oven and a large condenser, carry-

<sup>1</sup> Read before the American Institute of Mining Engineers.

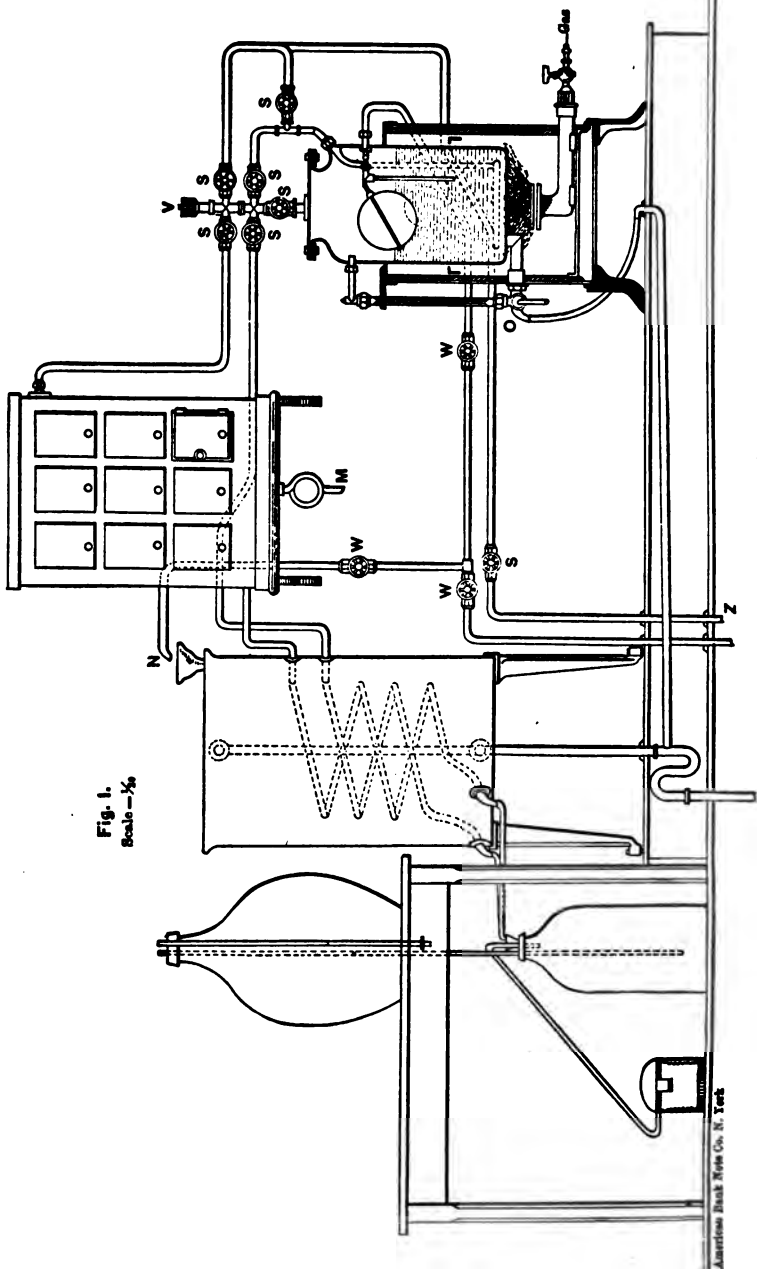


Fig. 1.  
Scale - 1/8

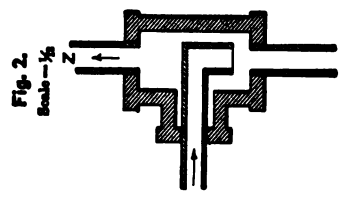


Fig. 2.  
Scale - 1/2

W. A. Morgan, Pat. 1109

A CONVENIENT STILL.

American Dist. Equip. Co. N. York

ing two block-tin worms, one direct from the still, the other from the oven, both delivering water to a carboy resting on the floor. When steam is taken from the large boiler, provision is made, by an arrangement seen in Fig. 2, located at Z, beneath the floor, to cleanse the steam, before it reaches the still, from the water mechanically carried into the pipes. The water returns to the boiler, while the steam passes to the still. By the arrangement of the steam-valves, S, it is possible to deliver the steam to the empty still, where it is again washed, and may then be passed either to the oven or direct to the condenser or to both. Or the steam from the boiler may be taken direct to the oven or to the condenser or to both. When a small quantity of steam is admitted to the still, most of the distilled water is condensed in the oven and is caught in a copper tin-lined vessel underneath, through the valve, M, a part passing to the condenser and then to the glass vessel, from which it may be forced to the carboy above. When there is no steam in the large boiler gas is used, the water being kept in the still at a constant level by the automatic arrangement before mentioned and seen in the sketch. In this case the steam may be passed to the drying oven or to the condenser direct or to both, as heretofore mentioned. In the case of gas alone, the still has a capacity of about twenty-six gallons of distilled water per day, while with steam from the boiler at a pressure of five pounds, I have made distilled water at the rate of 112 gallons per day. A convenient system of piping has been arranged for supplying water to the still and condenser, to the latter at N, and under control of valves, W, as seen in the sketch. The still and condenser are both connected with the waste, and may be emptied and cleaned when necessary. Other details of this apparatus are shown in the drawings. As I have used this still constantly for a year, and fully appreciate its merits and good points, I have no hesitation in recommending the design to those who may wish a still for the purpose for which this one is used.

## ON THE ESTIMATION OF THE EXTRACTION IN SUGAR HOUSES.<sup>1</sup>

BY M. TRUBEK.

Received September 9, 1895.

ONE of the most important things to be considered in the control of the work in sugar houses is the exact determination of the extraction, that is, the weight of juice obtained from 100 parts of cane. This is calculated in different ways. The raw juice, as it comes from the mill, passes through measured vessels before entering the clarifiers. From the number of the vessels filled or emptied during a certain time, the quantity of juice yielded by a certain weight of cane is determined. When working with dilution, the amount of diluting material has to be subtracted. Or the bagasse, yielded by a certain quantity of cane, is ascertained, and the weight of the cane minus the weight of the bagasse, gives the extraction.

The juice is generally measured directly in the clarifiers, and after making a correction in the volume for the higher temperature the juice has when it reaches the mark in the clarifiers, the per cent. dilution, if there is any; any other quantities added and reintroduced, as lime, syrup washings, etc., are deducted.

The determination of the extraction by this method offers some difficulties. Among others, some of the "quantities reintroduced" are hard to control; the mark in the clarifiers is often not easily seen on account of the foam on top of the juice. Moreover, the person in charge will have to take his figures, as quantity of lime in the different clarifiers, number of clarifiers filled during a certain period, amount of syrup settlings left in the syrup tanks and water used for washing them, etc., from the workingmen, who do not give them with the necessary exactness.

It would be of great value, therefore, if a method could be found to determine the extraction from data found in the laboratory only.

In case the juice was not diluted, the extraction can be figured from the fiber in the cane and that in the bagasse.

<sup>1</sup> Read at the Springfield meeting.

In 1865, E. Icery, in an article entitled "De quelques recherches sur le jus de la canne à sucre et sur les modifications qu'il subit pendant le travail d'extraction à l'île Maurice,"<sup>1</sup> admitting the inconveniences in the old method proposed to determine the extraction from the bagasse of the cane under operation; the fiber of the latter is either known or has to be found by analysis. He proceeds as follows:

Two hundred and fifty grams of the bagasse, (care being taken that the latter represent a good average sample), were quickly extracted with luke-warm water and then dried perfectly in a drying stove.

Let  $B$  = weight of the wet bagasse.

"  $B'$  = " " " dry "

"  $C$  = fiber in the cane.

"  $x$  = weight of juice extracted, then  $\frac{100 B'}{C}$  will represent the weight of cane yielding the amount of the wet bagasse  $B$ , and

$$1. \frac{100 B'}{C} - B = x.$$

The extraction  $y$  per 100 parts cane is then found according to

$$2. \frac{100 B'}{C} : x = 100 : y; \quad y = \frac{x C}{B'}.$$

If a determination of the fiber in the cane is not made, the author sets

$C = 10$  for: Belloughet (Java cane).

Diard.

and  $C = 11.5$  " : white or Tahitian.

Batavian.

Guingham (violet ribboned).

Penang.

The equations cited above (1 and 2) become simpler when calculating during the previous procedure the amount of dry bagasse per 100 parts of wet bagasse = fiber per cent. of bagasse.

I<sup>a</sup>.  $F_B : C = 100 : x$ ; II<sup>a</sup>.  $100 - x = E$ , where  $F_B$  = fiber in

<sup>1</sup> *Ann. chim. et. Phys.*, 5, 350-410.

bagasse;  $C$  = fiber in cane;  $x$  = bagasse yielded by 100 parts cane;  $E$  = extraction. Very often, in order to effect a more thorough exhaustion of the sucrose in the cane, water is allowed to run in fine streams on the bagasse, coming from the first set of rollers, and the resulting bagasse contains therefore a certain amount of water not belonging to the cane. In this case I determine the extraction in the following way:

If  $F_{B_1}$  = fiber in diluted bagasse,

$B$  = original bagasse corresponding to 100 parts of diluted bagasse,

$F_C$  = fiber in cane,

$x$  = bagasse resulting from 100 parts of cane,

$E$  = extraction,

we have the following equations:

$$1. \frac{F_{B_1} \cdot 100}{B} : F_C = 100 : x.$$

$$2. 100 - x = E.$$

The unknown figures are  $B$ ,  $x$ , and  $E$ , as  $F_{B_1}$  and  $F_C$  are found by analysis of the cane and its bagasse.

In order to find a third equation we determine the sucrose in the cane, the extracted juice and the resulting diluted bagasse.

Let  $s$  = sucrose in cane,  $s_1$  = sucrose in juice.

$s_{B_1}$  = sucrose in diluted bagasse.

In  $(100 - E)$  bagasse there is left  $\left(s - \frac{E s_1}{100}\right)$  sucrose, or in

$$100 \text{ bagasse } \frac{\left(s - \frac{E s_1}{100}\right) 100}{100 - E}.$$

We have therefore as the third equation:

$$3. \frac{\left(s - \frac{E s_1}{100}\right) 100}{s_{B_1} (100 - E)} = \frac{100}{B}$$

After eliminating we have

$$E = \frac{a}{2} \pm \sqrt{b + \left(\frac{a}{2}\right)^2}, \text{ where}$$



$$a = \frac{100 F_{B_1} (s + s_1) - 100 s_{B_1} F_C}{s_1 F_{B_1}}$$

$$b = \frac{10000 (F_C s_{B_1} - F_{B_1} s)}{s_1 F_{B_1}}$$

In the equation for  $E$  only the minus sign has to be taken.

Example :

Tons ground..... Nov. 29, 1894.  
1105

Dec. 1, 1894.  
1056

Regular feed on the carrier :

$F_{B_1} = 41.94$  ;  $F_C = 10.64$  ;  $s_1 = 10.95$  ;  $s = 9.785$  ;  $s_{B_1} = 4.80$ .

Substituting in the equation for  $E$  we have

$$E = 89.12 - \sqrt{-7824.05 + 7942.37}$$

$$= 78.25 \text{ per cent.}$$

It is obvious that in order to get good results extreme care must be taken to obtain an average sample of the cane and the bagasse, or the results will not represent the true facts. I will admit that it is not easy to obtain such an average sample and that exact methods for determination of the woody fiber and sucrose in cane and bagasse have not yet been found. In the future I will report more fully on this subject.

CHEMICAL LABORATORY OF RACELAND  
PLANTATION, RACELAND, LA.

## ON SILICIDES OF IRON.

BY G. DE CHALMOT.

Received September 23, 1895.

IRON and silicon readily unite at a high temperature. Silicides of iron of a definite composition have been made by Hahn.<sup>1</sup> He obtained compounds of the formula :  $\text{Fe}_3\text{Si}$ ,  $\text{FeSi}$ , and  $\text{FeSi}_2$ .

Since carbon readily reduces silica at the temperature of the electric arc, I expected to obtain silicides of iron with a large percentage of silicon by heating iron with silicon and carbon in an electric furnace. Iron filings, charcoal and sand were used and a silicide was obtained that contained from twenty-three to twenty-seven per cent. of silicon. In order to obtain this compound there must be an excess of sand and carbon. This com-

<sup>1</sup> *Ann. Chem.* (Liebig), 129, 57.

pound is white, crystalline, very hard, brittle and very little magnetic, the more so however if the percentage of silicon decreases. It conducts the electricity very well. In a pure condition it forms sometimes crystals of one cm. long. These crystals have the formula  $\text{Fe}_3\text{Si}_4$ .

	Calculated.		Found.
Silicon.....	25.04	25.17	25.30
Iron .....	74.96	74.75	....

The specific gravity is 6.36. This compound is very resistant against acid oxidizing agents. A sample of the silicide was ground and sieved through a 100 mesh sieve.

Cold aqua regia ( $\text{HNO}_3 + 3\text{HCl}$ ) dissolved by frequent stirring in two days 9.86 per cent., and in nine days 10.57 per cent. Of a sample of silicide containing 12.85 per cent. of silicon 66.84 per cent. was dissolved by the same reagent in two days. The commercial silicide of iron contained about eleven to thirteen per cent. of silicon, the original silicide contained 24.1 per cent. of silicon, that treated for nine days with aqua regia contained 27.2 per cent., which shows that only iron but no appreciable amount of silicon had been dissolved. The silicide is quite decomposed by hydrofluoric acid and also if it be melted with a mixture of sodium and potassium carbonate to which some potassium nitrate has been added.

Silicides of iron of great purity can be formed from impure materials like coke and river-sand. Iron ore may replace the filings.

I have also prepared in the electric furnace silicides of a higher percentage of silicon, *i. e.*, 29.3, 33.3, and 46.2 per cent.

These silicides seem to be mixtures of the compounds  $\text{Fe}_3\text{Si}_4$  and  $\text{FeSi}_2$ . The latter compound is described by Hahn as metallic greyish crystals.

The material richest in silicon which I obtained contained :

	Calculated for $\text{FeSi}_2$ .	Found.
Silicon .....	50.26	46.22
Iron .....	49.84	53.76

The specific gravity of this material was 4.851.. It was very brittle, crystalline, grey and nonmagnetic. Aqua regia dissolved in two days only 0.76 per cent. of the material that had been sieved through a 100 mesh sieve.

WILLSON ALUMINUM CO., SPRAY, N. C.

# ESTIMATION OF PHOSPHORIC ACID IN SOILS BY DOUBLE PRECIPITATION WITH MOLYBDIC SOLUTION AND TITRATION OF THE AMMONIUM PHOSPHO- MOLYBDATE WITH STANDARD ALKALI.

By C. B. WILLIAMS.  
Received September 30, 1895.

THE accurate estimation of the small quantities of phosphoric acid usually present in the acid extract of soils is a question that has given no small amount of trouble in soil analysis. There seems to be two main difficulties. First, in the precipitation with molybdic solution in the presence of large quantities of iron and aluminum salts, compounds of these latter elements are also often precipitated with the ammonium phosphomolybdate, and are either dissolved by the ammonia wash or remain in the cone of the filter as phosphates, thus giving rise to high or low results, as the case may be, unless special precautions are taken. In the second place very small quantities of phosphoric acid are not precipitated readily by magnesium chloride mixture and usually require long standing to be complete, in which case the precipitate is very liable to contain an excess of magnesia, thus giving rise to higher results.

Some work in the laboratory of the North Carolina Experiment Station upon the samples sent out by Prof. A. M. Peter, reporter of the A. O. A. C. on soils, indicate that these difficulties are readily overcome by the following procedure: The hydrochloric acid extract of the soil is obtained<sup>1</sup> by digesting the soil in acid of 1.115 sp. gr. at the temperature of boiling water and under atmospheric pressure for ten hours. The organic acid (one per cent. citric acid and 0.63 per cent. oxalic acid solutions) extracts<sup>2</sup> are obtained by digestion at laboratory temperature for five hours. Care must be taken to destroy all organic matter in the hydrochloric acid extract as well as in the organic acid extracts. This is done in the former case by adding about one cc. concentrated nitric acid for every three cc. of the portion taken for analysis and evaporating to two or three cc. concentration, and in the latter cases by evaporating the extracts to dryness and igniting with the addition of a small quantity of

<sup>1</sup> U. S. Dept. Agr. Div. Chem., Bul. 43, page 387.

<sup>2</sup> See report of A. O. A. C. Reporter on Soils for 1895.

nitric acid until organic matter is completely destroyed. These residues are now dissolved up to convenient volumes, and portions corresponding to eighteen, twenty or more grams of soil, and portions of the hydrochloric acid extract corresponding to one or more grams of soil (according to the richness in phosphoric acid) are precipitated, after adding about fifteen grams ammonium nitrate, at 40° C., with a large excess of molybdic solution, (thirty cc. is usually enough), let stand four hours, filter and wash with water twice. Now dissolve the precipitate into the beaker used for precipitation with dilute ammonia, wash the filter with dilute nitric acid and add concentrated nitric acid until precipitate begins to re-form; add ten grams ammonium nitrate, digest in water-bath at 65° C., add two cc. strong nitric acid with vigorous stirring, let stand five minutes, add two cc. molybdic solution, let stand eight minutes more and filter, wash and titrate according to volumetric method in this laboratory.<sup>1</sup>

The results presented in the table were obtained in the course of this investigation and show very close agreement with each other on the same solutions.

VOLUMETRIC DETERMINATION OF PHOSPHORIC ACID COMPARED WITH  
OFFICIAL GRAVIMETRIC METHOD.

No. of sample.	Official gravimetric method.	Hydrochloric acid solution.		Citric acid solution.		Oxalic acid solution.	
		First solution.	Second solution.	First solution.	Second solution.	First solution.	Second solution.
1	0.4505	0.4170	0.4069	0.0282	0.0290	....	0.0505
	....	0.4170	0.4069	0.0282	0.0287	....	0.0505
	....	0.4170	0.4069	0.0282	0.0287	....	0.0510
	....	0.4170	0.4069	0.0282	0.0287	....	0.0510
2	0.1720	0.1826	0.1826	0.0119	0.0146	....	0.0060
	....	0.1775	0.1826	0.0119	0.0146	....	0.0060
	....	0.1826	0.1928	0.0119	0.0146	....	0.0065
	....	0.1826	0.1928	0.0122	0.0152	....	0.0065
3	0.3956	0.3767	0.3867	0.0233	0.0255	....	0.0475
	....	0.3869	0.3867	0.0233	0.0255	....	0.0475
	....	0.3869	0.3867	0.0233	0.0255	....	0.0483
	....	0.3767	0.3818	0.0233	0.0261	....	0.0483
	....	0.3767	....	....	....	....	....
4	0.1932	0.3818	....	....	....	....	....
	....	0.1828	0.1929	0.0157	....	....	0.0087
	....	0.1878	0.1929	0.0157	....	....	0.0087
	....	0.1928	0.1929	0.0157	....	....	0.0087
	....	0.1878	0.1878	0.0162	....	....	0.0084

N. C. EXPERIMENT STATION, Raleigh, N. C.

<sup>1</sup> See description of volumetric methods in methods of the A. O. A. C. for 1895.

## ON THE USE OF ORGANIC BASES IN THE PREPARATION OF BARIUM AND CALCIUM FERROCYANIDES.

BY PERCY H. WALKER.

Received October 21, 1895.

THE methods hitherto proposed for the preparation of ferrocyanides of barium and calcium are based either upon the decomposition of Prussian blue by the hydroxides of barium or calcium; or upon double decomposition of barium or calcium salts on the one hand, and potassium ferrocyanide on the other.

It is very difficult to prepare Prussian blue free of potassium, and the double ferrocyanides of barium or calcium with potassium are formed more readily than the simple salts. Even when the simple salts are formed, if any potassium salt has been used in the preparation, it is almost impossible to remove the whole of the potassium by recrystallization.

After trying various other methods for the preparation of barium ferrocyanide, and having very poor success, I undertook, at the suggestion of Dr. Launcelot Andrews, to prepare it according to the following method:

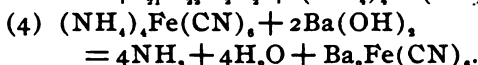
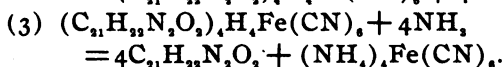
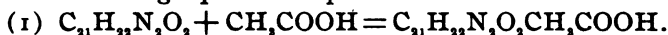
This method depends upon the formation of the normal strychnine ferrocyanide, the decomposition of this with ammonia, and the decomposition of the ammonium ferrocyanide by means of barium hydroxide. Strychnine was converted into the acetate by gently heating with water and the calculated amount of acetic acid. This salt, though one of the most soluble salts of strychnine, readily separates in the crystalline form from comparatively dilute solutions when allowed to cool, so it is best to keep it warm. A solution of the calculated amount of potassium ferrocyanide was added to the strychnine acetate, allowed to stand in a warm place, stirred frequently, and the white crystalline strychnine ferrocyanide, filtered and washed. After washing, the strychnine ferrocyanide was thoroughly mixed with ammonia water in excess, which decomposed it forming ammonium ferrocyanide and precipitating strychnine, which was easily separated from the solution of ammonium ferrocyanide, and could be used over again.

The solution of ammonium ferrocyanide, with excess of ammonia, was then boiled with a solution of the calculated

amount of barium hydroxide until no more ammonia was given off. The solution was allowed to cool, decanted from the crystals, and the mother liquid further evaporated. The crystals were dried in the air. They were found to contain a very slight amount of barium carbonate. On analysis, they gave 9.43 per cent. of iron and 46.98 per cent. of barium, which corresponds very closely to a salt of the composition represented by the formula  $\text{Ba}_2\text{Fe}(\text{CN})_6 \cdot 6\text{H}_2\text{O}$ , and which is described in Wurtz Dict. de Chim., p. 1090.

The barium ferrocyanide can be easily prepared by this method. The main objections to this method are the bulk of liquid required to dissolve the strychnine salt, and the chance for the formation of barium carbonate during the boiling of the ammonium ferrocyanide solution with barium hydroxide. This last objection can be largely avoided by boiling in a large flask, not with the direct flame, but by passing in a current of live steam. This latter method also has the advantage of inducing the formation of better crystals of barium ferrocyanide.

The following equations represent the reactions :



Quinoline ferrocyanide was prepared in a similar manner, and this was treated directly with barium hydroxide solution, and the attempt made to get rid of the quinoline by distilling. A large amount of Prussian blue was formed, however, and the mass was thrown away. No other attempt was made using quinoline, as it was then thought that dimethylaniline would answer.

This latter method is the easiest tried and leaves little to be desired. Dimethylaniline is mixed with water, and hydrochloric acid added in slight excess. This solution then mixed with potassium ferrocyanide solution, the whole filtered and the precipitate washed with the least possible amount of water, then with alcohol, and finally with ether, and dried between pieces of filter-

paper. As little water as possible must be used, as the salt is rather soluble.

#### ANALYSIS OF THE DIMETHYLANILINE SALT.

Into a beaker was put 0.2220 gram with about one gram pure calcium carbonate, titrated with standard silver nitrate (one cc. = 5.829 milligrams sodium chloride) using potassium chromate as indicator. Required 18.4 cc. The end reaction was not very sharp, and after standing over night the red color disappeared. Then added more of the silver solution, making a total of 19.5 cc. One cc. of the above silver nitrate solution would be equivalent to 11.26 milligrams di-acid dimethylaniline ferrocyanide. Therefore the 19.5 cc. would correspond to 0.21957 gram.

Taken, 0.1325 gram mixed with water and two cc. dilute sulphuric acid added. Then added 17.18 cc. silver nitrate solution and two cc. solution of iron alum, titrated back with solution of potassium thiocyanate corresponding to the silver nitrate solution. Required six and one-tenth cc. Therefore 11.08 cc. silver nitrate solution used up by salt. In this the end reaction was not sharp.

Taken, 0.1341 gram salt. Treated as above except filtered before titrating back silver nitrate. Sixteen cc. silver nitrate added, four and one-tenth cc. potassium thiocyanate required. Therefore 11.9 cc. silver nitrate solution used, which corresponds to 0.1340 gram of the di-acid salt.

Mixed 0.1350 gram with water and titrated with tenth normal sodium hydroxide, using phenolphthalein as indicator.

Required twelve cc. which corresponds to 0.1351 gram of the di-acid salt.

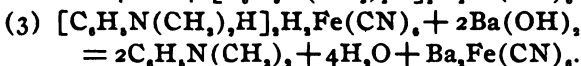
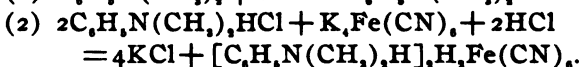
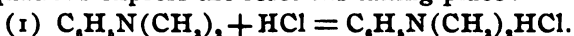
The compound is, therefore, the di-acid dimethylaniline ferrocyanide  $[C_6H_4N(CH_3)_2H]_2Fe(CN)_6$ , a white crystalline salt, which is somewhat soluble in water.

#### PREPARATION OF BARIUM FERROCYANIDE BY THE DIMETHYLANILINE FERROCYANIDE METHOD.

30.5 grams di-acid dimethylaniline ferrocyanide is mixed with barium hydroxide solution containing 22.5 grams barium hydroxide and shaken violently for some time in a flask or separatory funnel. Most of the barium ferrocyanide crystallizes out

directly and can be filtered from the liquid. The dimethylaniline is recovered by shaking the liquid with ether, which also causes more of the barium ferrocyanide to separate.

The crystals of barium ferrocyanide should be well washed, first with a little water and then with alcohol. The following equations express the reactions taking place :



Barium ferrocyanide  $[\text{Ba}_2\text{Fe}(\text{CN})_6 \cdot 6\text{H}_2\text{O}]$  crystallizes in oblique rectangular prisms belonging to the monoclinic system. The crystals are unaltered in the air at ordinary temperature, lose eleven-twelfths of their water at  $40^\circ \text{C}.$ , the rest of the water is not driven off until the salt begins to decompose. The solubility varies from one in 584 parts cold water to one in 116 parts boiling water.<sup>1</sup> Dammer gives the solubility as varying from one in 1000 parts water at  $15^\circ$  to one in 100 at  $75^\circ$ .

#### SOLUBILITY OF BARIUM FERROCYANIDE.

Some solubility determinations were made on the salt prepared as above. The apparatus used was, I believe, devised by Dr. Launcelet Andrews. The apparatus consists of two Woulff bottles, *A* and *B*. *A* has three necks. The middle neck contains a perforated stopper holding a thermometer, the bulb of which goes nearly to the bottom of the bottle. The left hand neck has a stopper carrying a short glass tube which can be connected with the suction pump. The right hand neck has a stopper with a tube passing through and reaching to the bottom of the bottle; in fact, it is better to have the tube touch the bottom. This tube is connected to a tube passing through one of the necks of *B*, the other neck of *B* has a tube passing nearly to the bottom of the bottle. Water is put in the two Woulff bottles, and in *A* a larger amount of the salt to be tested than can be dissolved by the water. The whole apparatus is then put in a vessel of water, and air drawn through for several hours. The water in *B* preventing any evaporation from *A*. The current of air is then

<sup>1</sup> *Wurtz Dict. de Chim.*, p. 1091.



stopped long enough to allow the undissolved portion to settle. A measured amount of the clear liquid taken out, noting the temperature, evaporated and residue weighed.

	Amount solution.	Tempera- ture.	Residue. grams.	Parts water.	
I.	5 cc.	18° C.	0.0194	257.7	
II.	5 cc.	18° C.	0.0198	252.5	
III.	30 cc.	18° C.	0.1190	252.1	Added 50 cc.
IV.	25 cc.	17° C.	0.0936	267.0	Water to A.
V.	25 cc.	19° C.	0.0930	268.8	
VI.	25 cc.	16° C.	0.0924	270.5	

These results fall within the limits as given by Wurtz.

#### PREPARATION OF CALCIUM FERROCYANIDE.

Twenty-three grams of di-acid dimethylaniline ferrocyanide mixed with water and milk of lime prepared from six grams pure lime. The mixture shaken violently in a flask, allowed to stand some time, filtered, shaken with ether to separate the dimethylaniline, separated from ethereal solution with separatory funnel, evaporated down in flask, carbon dioxide passed through, again boiled, filtered, and evaporated to about fifty cc. Alcohol then added, which causes crystals to separate. Then crystals dried between filter-paper. The crystals are of a pale yellow color and are very soluble in water. When a saturated solution is allowed to stand for a long time at the temperature of the laboratory, large flat crystals are deposited.

#### NOTE ON THE SEPARATION OF IRON AND ALUMINUM.

Since strychnine ferrocyanide is almost insoluble and is easily filtered, it may possibly be used to separate iron and aluminum in the following manner:

The solution containing ferric and aluminum salts is treated with excess of strychnine ferrocyanide. The Prussian blue thus formed can be filtered with ordinary filter-paper and the aluminum precipitated by ammonia from the filtrate. By this method I have easily gotten perfectly white aluminum oxide; but have not as yet gotten the conditions for a complete quantitative separation.

I wish in conclusion to express my thanks to Dr. Launcelot Andrews, who, by his advice and assistance, rendered this work possible.

## ON THE FORMATION OF LAYERS IN MIXTURES OF ACETIC ACID AND BENZENE.

By C. E. LINEBARGER.

Received October 21, 1895.

DUCLAUX<sup>1</sup> states in reference to mixtures of benzene and acetic acid that "at temperatures from 15°–20° these two liquids are soluble in every proportion with each other. If a mixture of equal volumes of the two substances be cooled to about 11°, the mixture, until then homogeneous, becomes troubled all of a sudden and separates into two nearly equal layers; 0.2° of interval of temperature at most separate the two states." Duclaux then proceeds to give the results of his analyses of the two layers, as well as other results and discussions.

This account has been universally accepted, and it has passed into standard text-books that mixtures of benzene and acetic acid present at certain temperatures the phenomenon of layer-formation. This is not, however, according to fact; mixtures of *very pure* acetic acid and benzene do not separate into layers even at temperatures as low as 20°. Duclaux's observations were not made on binary mixtures of acetic acid and benzene, but upon *ternary* mixtures of *water*, acetic acid, and benzene.

A certain theoretic importance attaches itself to this question. In the course of an investigation of the vapor-tensions, both partial and total, published a few months ago in this Journal, the results found with mixtures of benzene and acetic acid were such as to preclude the possibility of layer-formation in this case. Accordingly, I have carried out some experiments on the exposure of mixtures of acetic acid, benzene, and water to varying temperatures to ascertain under what conditions of concentration and temperature, layer-formation takes place.

A cylindrical phial provided with a good cork was filled about two-thirds full of mixtures of acetic acid<sup>2</sup> and benzene.<sup>3</sup> The tube was enclosed in another larger tube, so as to prevent any possible contamination of the contents of the first tube with the baths or freezing mixtures. Several mixtures of different concentrations were exposed to a temperature of –20°, but in no case did there occur a separation into layers.

<sup>1</sup> *Ann. chim. phys.* [5], 7, 267, 1876.

<sup>2</sup> Purified by repeated crystallization until melting-point was not perceptibly changed no matter what the relative proportions of solid and liquid acid was.

<sup>3</sup> Purified by repeated treatment with strong sulphuric acid, repeated crystallizations and distillation over sodium.

14.6225 grams of a mixture containing 7.6037 grams of acetic acid and 7.0188 grams of benzene were placed in the tube described above and a few centigrams of water were added successively, the mixture being exposed to the temperature of a mixture of ice and salt, *i. e.*, about  $-20^{\circ}$ , after each addition of water. Not until 0.7226 gram of water had been added did there occur a separation into layers, which persisted even at  $0^{\circ}$ , but disappeared a few degrees above.

Now, Duclaux was fully aware that the presence of water rendered it possible to cause layer formation even at temperatures above  $11^{\circ}$ , for he writes: "It is indeed not necessary to have recourse to cold to obtain the separation, and the state of unstable equilibrium in which these liquids are, can be destroyed by the addition of a third substance, as, for example, water.

"A single drop of water suffices to cause a mixture of 10 cubic centimeters of benzene and of 10 cubic centimeters of acetic acid to become troubled.

"Acetic acid crystallizing at  $14^{\circ}$  always gives a limpid solution with benzene. If it crystallizes only at  $12^{\circ}$  the mixture of equal volumes remains troubled."

Now, acetic acid melting at  $14^{\circ}$  contains not inconsiderable quantities of water, so that the behavior just described by Duclaux is what is to be expected under the circumstances. If Duclaux had taken the trouble to raise the melting-point of his acid by a few fractional crystallizations, and had employed this purified acid, there would have been one less error and its rectification encumbering the pages of chemical journals.

#### SCHEME FOR THE IDENTIFICATION OF ACETANILIDE, PHENACETINE, QUININE SULPHATE, ETC.

By F. S. HYDE.

Received October 29, 1895.

THE test made by boiling the substance with caustic potash and chloroform is one of the most important in the scheme given below. It is known as the "carbylamine reaction" or "isonitrile test," and is common to those compounds which are classed as *primary amines* ( $R-NH_2$ ).



SCHEME FOR THE IDENTIFICATION OF ACETANILIDE, PHENACETINE, QUININE SULPHATE, ETC.

Pure substance.	Melting-point. C.	Solubility in water.	Boiled with excess caustic potash and few drops chloro- form.	Solution of substance in water.		
				Ferric chloride.	Dilute nitric acid.	Bromine water.
Acetanilide (Phenyl acetamide) $C_6H_5NH_2COCH_3$	113°	Soluble in cold ; more so in hot.	Odor of isonitrile.	Yellow solution. Red on boiling.	Colorless.	White crystals. Para-brom- acetanilide.
Exalgine (Methyl Phenyl acetamide) $C_6H_4N(CH_3)COCH_3$	101°	Not very soluble, cold ; easily solu- ble, hot.	No odor of iso- nitrile. Class of secondary amines.	Yellow solution. Cloudy red on boil- ing.	Colorless.	No precipitate.
Phenacetine (Acetylparaamidophenetol) $C_6H_4OC_2H_5NH_2COCH_3$	135°	Soluble with difficulty.	Odor of isonitrile.	Yellow solution. Blood-red on boil- ing.	Cloudy yellow solution. Crystals of nitro compound.	No precipitate.
Phenecoll hydrochloride (Glycocolparaamidophene- tol) $C_6H_4 < \begin{smallmatrix} OC_2H_5 \\ NH_2COCH_3 \end{smallmatrix} NH_2.HCl$	No. M. P. HCl Comp.	Very soluble.	Odor of isonitrile.	Yellow solution. Darkens and orange precipitate on boiling.	Colorless.	No precipitate.
Salol (Phenol salicylate) $C_6H_4.OH.COOC_6H_5$	43°	Soluble with difficulty.	No odor of iso- nitrile. Yellow solution.	Yellow solution. Blood-red on boil- ing.	Colorless.	No precipitate cold ; white cloudy compound on boil- ing.
Resorcin (Metadioxybenzene) $C_6H_4(OH)_2$	118°	Easily soluble.	No odor of iso- nitrile. Carmine-red solution.	Dark violet. Yel- lowish on adding drop of sulphuric acid.	Yellow solution.	Yellowish precipi- tate dissolving im- mediately.
Quinine sulphate $C_{20}H_{24}N_2O_5.H_2SO_4$	....	Slightly soluble. With few drops of sulphuric acid dis- solves with blue fluorescence.	Base precipitates and dissolves on heating.	Yellow solution.	Colorless with blu- ish fluorescence.	Dry substance on porcelain with weak bromine water gives green coloration on add- ing two or three drops ammonia water = Thalleo- quin test.
Antipyrine (Phenyldimethylpyrazolon) $HOC_6H_3(CH_3)_2C_6H_5$	113°	Soluble.	Nothing.	Blood-red. Disap- pears on adding a drop of sulphuric acid.	Colorless.	Yellowish-white precipitate.

*Phenacetine*.—Contrary to some writers, phenacetine *will* give the isonitrile test, and hence cannot be distinguished from acetanilide by this reaction.<sup>1</sup>

Exalgine does not respond to this test because it is a *secondary* amine; hence a distinction from acetanilide, phenacetine, and phenocoll.

The odor of raspberries attributed to exalgine, when heated, is somewhat misleading. It is certainly aromatic, but may resemble either strawberries or mulberries.

By boiling acetanilide with an alkaline solution of sodium hypobromite (NaBrO) or with alkaline permanganate, the same odor of isonitrile is produced, but the reaction is complicated and not perfectly understood. However, it is assumed that the benzene ring constituting the nucleus of the compound is partially broken down by the strong oxidizing action of the hypobromite or permanganate, and thus furnishes the necessary carbon substitution in the formation of isonitrile.

In making the carbylamine, isonitrile, or "isocyanide" test, as it may be called, it is preferable to have the solution strongly alkaline in every case to insure a more complete decomposition as well as quicker reaction and a more perceptible odor.

---

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

## ON THE PHYSICAL AND CHEMICAL PROPERTIES OF SOME CALIFORNIA OILS.

BY WALTER C. BLASDALE.  
Received September 13, 1895.

THE investigations of which I would here record the results were undertaken some two years ago with three definite objects in view; first, the accurate determination of the limits of some of the standard constants of California olive oils; second, a practical test of the application of the Babcock method of determining adulterants in butter to a similar purpose for olive oil, and finally a determination of some of the constants of three new and hitherto undescribed oils of vegetable origin. In carrying out this work I have followed in general the methods laid down by Allen for the examination of oils, introducing such

<sup>1</sup>*J. Anal. Appl. Chem.*, 7, 354.

modifications as more recent investigations have shown to be advisable.

The oils which have been used comprise the following samples:

1. Eleven samples of pure olive oil prepared under my own supervision from six standard varieties of olives, *viz.*, Pendulina, Uvaria, Rubra, Redding Picholine, Nevadillo blanco, and Manzanillo, according to the usual method of preparing oil for the market in California. The essential difference between the samples marked "first" and those marked "second" is that the latter include oil from the pits as well as from the pulp of the olives. A small amount of warm water was added to the pomace before pressing in the latter case. These oils, as received from the press, were washed repeatedly and filtered until clear.

2. Two samples of mustard-seed oil of California manufacture.

3. One sample of oil from the kernel of the English walnut (*Juglans regia*) grown in the southern part of the state. This oil was prepared by extraction with petroleum ether.

4. One sample of oil prepared from the fruit of our live-oak (*Quercus agrifolia*) by extraction with petroleum ether. This yields a deep brown fluorescent oil, which readily solidifies at a temperature of 10° C, and on long standing deposits waxy masses.

5. Oil prepared from the pine-nuts (probably the fruit of *Pinus monophylla*) found in our markets. This is a brown drying oil of a rather unpleasant odor and taste.

6. Oil prepared by Mr. V. K. Chesnut, from the fruit of the California nutmeg (*Tumion Californicum*).

7. Ten samples of the salad oils commonly sold in our groceries, comprising the following brands:

1. "Pure Olive Oil," J. Revalk, San Francisco.

2. "Pure California Olive Oil, Alpha Brand," Merriman Mfg. Co.

3. "California Olive Oil," Merriman Mfg. Co.

4. "Sierra Madra Olive Oil," Goldberg, Liebenbaum, and Bowen, San Francisco.

5. "Coburn's Pure Olive Oil," C. W. Coburn, San Francisco.

6. "Extra Quality Oil, Huile Vierge," A Durand et Fils, Bordeaux.
7. "Fine Salad Oil," Franco American Oil Co.
8. "Cooper's California Olive Oil."
9. "Huile D'Olive Superfin," F. Aristoy, Bordeaux.
10. "Huile Vierge," De Bossel Fil's, Marseilles.

The determinations and special tests to which these were subjected are as follows:

*Specific Gravity.*—This was in all cases determined by an accurately standardized pycnometer of about fifty cc. capacity.

*Index of Refraction.*—Determined by an Abbe refractometer of the Zeiss pattern.

*Thermal Degree.*—By this I mean the increment of temperature resulting from mixing fifteen cc. of oil with five cc. of concentrated sulphuric acid in a calorimeter with constant stirring, using an initial temperature of at least 20° C. This method of carrying out the test was rendered necessary by the small quantities of many of the samples available; as the test is of no value except when compared with known oils this forms no serious objection to the results here presented. It is perhaps unnecessary to state that the same sample of acid was used in all the tests.

*Viscosity Test.*—I believe Prof. Rising was the first to suggest the possibility of using the factor representing the viscosity of the soap formed from a standard amount of oil in detecting adulterated olive oil. At his suggestion Mr. Babcock made the test with a number of samples of commercial oils, the results of which agreed entirely with those obtained by the application of standard tests to the same series of oils.<sup>1</sup> The method which I have used, which is essentially the one adopted by Mr. Babcock, is as follows: Fifteen grams of oil are placed in a saponification flask with about thirty cc. of water containing exactly seven and a half grams of potassium hydroxide and ten cc. of alcohol and heated on a water bath until complete saponification has been effected. The resulting soap is washed into a large evaporating dish, heated until the alcohol is expelled, diluted to exactly 500 cc. at 15° C., and the viscosity of the resulting solu-

<sup>1</sup> Methods of Detecting Adulterations in Olive Oil. Report of Olive Grower's Convention, held in San Francisco, July, 1891.

tion determined by means of a torsion viscometer, the results being calculated in terms of the number of grams of sugar which it would be necessary to add to a liter of water in order to produce a solution of equal viscosity. In the case of the two mustard-seed oils, it was found necessary to dilute the solution to one liter in order to obtain a workable solution. My more recent experiences would induce me to make some few changes in this process, the most important of which would be a change in the working temperature from 15° to 20° C.

*Saponification Number.*—By this I mean the number of milligrams of caustic potash required to saponify one gram of oil. It has been determined by the standard method, operating upon two and one-half grams of oil.

*Iodine Absorption.*—For this determination I used the standard method of Hübl, basing the standard of the hyposulphite solution on pure potassium bichromate according to the method of the Association of Official Agricultural Chemists.

*Melting Point of Fatty Acid.*—For the determination of this constant I found it most satisfactory to prepare thin but wide glass tubes on the side of which a drop of the fatty acid is allowed to solidify. This is then attached to the bulb of a thermometer, placed in a water-bath and heated until a temperature is reached at which the fat begins to run down the side of the tube. Even when the greatest care is used considerable variations will be found in the results obtained from the same sample of oil.

*Elaidin Test.*—In this I have followed the method of Poutet, the one based on the use of a freshly prepared solution of mercurous nitrate. The time required for the production of a good elaidin varies considerably, and I have indicated this factor somewhat roughly in the accompanying table.

*Milliau's Test.*—The test proposed by that author and described in this Journal, 15, 153.

An inspection of the accompanying table will show that most of the constants obtained for the pure olive-oils agree fairly well with those obtained for European oils. The iodine absorption, however, is exceptional since many of the results here reported are higher than the commonly accepted European standards.





A possible explanation may be found in the fact that many of the varieties here represented are not those commonly used for the production of oil. Similar results have been obtained by Mr. G. E. Colby.<sup>1</sup> In the application of the elaidin test striking differences were observed both in the character of the elaidin and in the length of time necessary for its production. On the one extreme are oils of the Manzanillo type which produce a perfectly solid mass within an hour, whereas the two Uvaria oils produced only a partial solidification even after six hours. The facts seem to indicate that the test is not as reliable as has been supposed.

From a comparison of the results obtained from the oils of known purity with those obtained from the commercial oils it will at once be seen that Nos. 18, 23 and 24 are heavily adulterated with cottonseed-oil. No. 20 shows strong evidences of adulteration though the percentage is not as high as in the other cases.

I think it is also shown that the application of the viscosity test to the detection of adulterated olive oils is entirely successful; the variations in the figures obtained from the different samples of pure oil are considerable but not so great as to admit of confusion with any of the adulterated oils. In addition to the figures presented in the table, I have obtained the following results: For cottonseed-oil 280, for sweet-almond oil 645, for rape-seed oil 670, for poppy-seed oil 95, for sesame oil 415, for lard oil 250, and for peanut oil 220, an array of figures which plainly shows the utility of this test. It will be seen that the only oils whose viscosity-constant approaches that of pure olive oil are almond, rape-seed and sesame. Of these the first is not likely to be used as an adulterant and the two latter are readily detected by other tests. The only oils showing a materially higher viscosity constant are the two mustard-seed oils, and it must be admitted that carefully proportioned mixtures of mustard and cottonseed-oils could not be detected by this test. The method promises to be of particular value in detecting lard oil for which we have had no satisfactory specific test.

Of the three hitherto undescribed oils No. 16 seem to agree in

<sup>1</sup> Report of California Agricultural Experimental Station, 1890.

most of its properties with other oils prepared from related plants, viz: *Pinus sylvestris*, *Pinus picea*, and *Pinus abies* in so far as these are known, and could probably be used for similar purposes.

No. 17 though obtained from a closely allied plant is an oil of quite a different character, but the data at present available is too insufficient to admit of a satisfactory prediction of its constituents. It might be of interest to note here that J. J. Rein, in a work entitled "The Industries of Japan," mentions the fact that an oil is prepared by the Japanese from the fruit of *Tumion nucifera* and used by them in their kitchens.

In conclusion I wish to express my thanks to Prof. Rising for suggestions received during the course of the work and also to the officials of the Experiment Station at Berkeley, through whose kindness I was enabled to obtain the samples of pure olive oil.

#### THE DETERMINATION OF PHOSPHORIC ACID BY THE MOLYBDATE-MAGNESIA METHOD, AND BY VOLUMETRIC METHOD.<sup>1</sup>

BY B. W. KILGORE.

Received September 30, 1895.

IN a summary statement of the results obtained last year by the members of the Association of Official Agricultural Chemists and other chemists cooperating with them by the official molybdate method on a solution of C. P. disodium hydrogen phosphate, I called attention<sup>2</sup> to the fact that the results of nearly all of the analysts (twenty-eight) were high and some of them very materially so. The larger number of these analysts were experienced in this class of work. From this and other reasons I argued that the molybdate method, as usually worked, has a tendency to give high results, and that these high results are due to an excess of magnesium in the magnesium ammonium phosphate precipitate.

For the investigation of phosphoric acid methods for this association for 1895, two chemically pure phosphate solutions and one mixed fertilizer were employed.

<sup>1</sup> For description of this method, see methods of the Association of Official Agricultural Chemists for 1895.

<sup>2</sup> This Journal, 16, 793.

No. 1 was a solution of the same phosphate worked upon last year, and contained ten grams chemically pure disodium hydrogen phosphate to the liter, the theoretical percentage of phosphorus pentoxide in this salt being 19.826.

No. 2 was No. 1 diluted with five parts of water, and therefore contained the equivalent of 3.304 per cent. phosphorus pentoxide in 50 cc.

Fifteen chemists reported forty determinations on solution No. 1, the highest of which was 20.50 per cent., and the lowest 19.75 per cent., the former being 0.674 per cent. above the theory, and the latter 0.076 per cent. below. The average of all results was 20.044 per cent., or 0.218 per cent. above the theoretical content; the variation between the highest and lowest results was 0.75 per cent.; the variation below the theory was 0.076 per cent., and above the theory 0.674 per cent. Fourteen per cent. of the determinations were within 0.05 per cent. of the theory; thirty-three per cent. within one-tenth; and fifty-six per cent. within two-tenths. On the whole these results make a slightly better showing toward accuracy than did those of last year on the same phosphate, but like the results of last year, most of them are high. In 1894 there were two results below the theory, 19.74 and 19.78 per cent.; this year there are also two, 19.75 and 19.77, the lowest of the former being 0.08, and of the latter 0.07 per cent. below the theory; while the highest results of the two years were 0.84 and 0.76 per cent. above the theory.

On sample No. 2, containing 3.304 per cent. phosphorus pentoxide, there were forty-two determinations reported, the highest of which was 3.65 per cent., or 0.346 per cent. above the theory; and the lowest was 3.20 per cent., or 0.104 per cent. below the theory. The average of all results was 3.43 per cent., or 0.126 per cent. high. Out of forty-two results on this sample, four were below the theory. These variations being 0.10, 0.02, 0.02, and 0.01 per cent.

The foregoing adds strength to the remarks made on this subject last year, that the molybdate-magnesia method gives high results in the hands of nearly all workers, and may give extremely high ones in the hands of some.

We do not believe, however, that there is any well established

method of sufficient rapidity that suits our needs better or with which we can get better results, when proper precautions are taken, than the molybdate method.

It may be of interest here to give also a brief summary of the results on these same phosphate solutions by the volumetric method as investigated this year. The results were obtained by some of the same chemists who analyzed these samples by the gravimetric method. This was the first time the volumetric method in its present form had been used by most of them.

Thirteen chemists reported thirty-one determinations on solution No. 1 and thirty-three on No. 2 by the volumetric method. Seventy-three per cent. of all the results on No. 1 were within 0.05 per cent. of the theory, and ninety-three per cent. were within one-tenth per cent., there being only three results varying more than one-tenth. On sample No. 2 eighty-five per cent. of the results were within 0.05 per cent. of the theory, and all were within one-tenth.

The results upon which the foregoing discussion is based will appear in the proceedings of the A. O. A. C. in the "Report on Phosphoric Acid," made by the writer to that association at its recent meeting.

NORTH CAROLINA EXPERIMENT STATION,  
Raleigh, N. C.

## THE VOLUMETRIC ESTIMATION OF MANGANESE.

BY GEORGE AUCHY.

Received October 22, 1895.

IN this Journal, 17, 5, Mr. W. H. Thomas describes his experience with Low's and with Volhard's method of determining manganese. The latter he finds reasonably accurate. The former not at all so. Some ten or twelve years ago, in the transactions of the American Institute of Mining Engineers, Williams' method in steel, which is based on the same principle as Low's method in ores, was the subject of considerable controversy; some claiming, others disputing its accuracy. And although the weight of the testimony seemed to be in favor of the method, nevertheless, the close of the discussion left the matter still somewhat in doubt.

Are methods based upon this principle reliable? Mr. Thomas'

experience with Low's method is further evidence to the contrary. But as regards Williams' method, perhaps it may be said that Mr. Thomas' results are not in evidence, inasmuch as potassium chlorate and strong nitric acid are stronger oxidizing agents than bromine water, and may therefore be depended upon to oxidize the manganese completely to manganese dioxide, even if the latter cannot be. But Mr. Stone's and others work is against this assumption; also the following results obtained from manganese ores:

Ore No.	Williams' method (practically) per cent.	Volhard's method. per cent.
1.....	51.71	53.04
" " 2.....	51.58	53.00
" " 3.....	44.88	46.80
" " 4.....	43.00	46.24
" " 5.....	41.22	42.64
" " 6.....	34.39	40.00
" " 7.....	44.88	46.40
" " 8.....	31.61	43.76

Among steel works chemists, Williams' method is very popular on account of its great ease and simplicity. Comparatively few, perhaps, use Volhard's method. And it is therefore important that the reliability of the former method be more fully and definitely established. So far, the evidence in its favor is strong and positive. But there is still room for doubt. More work seems to be required to fully settle the question, and it would be well for chemists who use this method, to patiently check with Volhard's method for a considerable time, (using different lots of chlorate) and communicate their results and opinions to the Society. I say Volhard's method, because the gravimetric is too cumbersome for such an extended use, and is probably moreover not any more accurate—perhaps not so much so—as Volhard's.

My own experience with Williams' method leads me to believe that it usually, but not always, gives accurate results. And I am disposed to think that if chemists who have repeatedly obtained good results with that method, and who have therefore every confidence in it, would nevertheless keep on for an extended period checking their results by Volhard's method

they would sooner or later be treated to a disagreeable surprise such as illustrated by the last four of the following results :

	Williams' method, per cent.	Volhard's method, per cent.
Heat ..... 114	0.42	0.42
Rolled steel..... ...	0.43	0.45
Heat ..... 116	0.50	0.50
" ..... 120	0.40	0.41
" ..... 121	0.42	0.42
Tire steel..... ...	0.92	0.94
Heat ..... 125	0.48	0.54
Tire ..... ...	1.04	1.20
Heat ..... 162	0.37 and 0.42	0.45
" ..... 163	0.40	0.48

With heat 163 Williams' method was given up.

With regard to the method of oxidizing to permanganate by lead oxid and titrating with arsenious solution, without having given the method actual trial, I am nevertheless convinced that it gives uniformly low results, from the fact that while it was in use at these works, 135 and 140 pounds of ferromanganese per charge was needed to bring the manganese content to the required point, working by this method, while now, with Volhard's method in use, only ninety and 100 pounds are used to bring the same result. But the lead oxid used in the method was the tetroxide. Probably by the use of dioxide, good results may be obtained.

For the benefit of chemists, who have never used Volhard's method, and who feel disposed to give it a trial, for the purpose I have suggested, I beg to call attention to certain precautions which are essential to a successful practice of the method.

1. In boiling off the nitric acid with sulphuric acid, it is very essential to avoid too much sulphuric acid, as otherwise the bumping and spattering will be so violent as to altogether spoil the test.

2. The dry mass should be taken up with *hot* water, allowing the dish first only a minute or two for cooling. If the dish be allowed to cool completely, and cold water be added, and then boiled up, very frequently a red ferric sulphate carrying much manganese will remain insoluble, no matter how much additional sulphuric acid be added. Even this precaution is value-

less, however, if the dry mass be heated too long. But this residue can be brought into solution by decanting the clear solution and then heating for some time with sulphuric acid. But to save time its separation should of course be prevented in the first place.

3. In steels high in manganese it is advisable, and in steels low in manganese it is absolutely essential that not too much zinc oxide be used; as it will separate out when the solution is heated, if much has been used, and will retard the settling of the manganese dioxide if the steel be high in manganese, and will completely prevent it if the steel be low in manganese, (0.18—0.24 per cent.) and thus make the observation of the end of the titration impossible. Before the zinc oxide is added, therefore, the solution should be in as small a bulk as convenient and be as nearly neutralized with sodium carbonate as possible.

4. When titrating with permanganate, the reddish color caused by the permanganate should be completely changed into clear yellow by shaking the flask before more permanganate is added, and at the end the liquid must be distinctly and permanently rose colored—that is, it must retain its color through a dozen good shakings. It is well, toward the end, to add the permanganate four drops at a time (when two drops equal one-tenth cc.) till the distinct rose-tint is reached, and then deduct one-tenth cc. from the reading of the scale.

It may be a convenience to state the method in detail. Take exactly three and three-tenths grams in a six-inch evaporating dish. Cover and dissolve on the hot plate in forty cc. of nitric acid containing a little more than half of strong acid. Add eight cc. (no more) strong sulphuric acid. If, however, the liquid becomes cloudy on boiling, the violent bumping and spattering before referred to will inevitably occur as the boiling progresses further. Add then at once some strong hydrochloric acid, and transfer to a wire gauze, where boil down rapidly over a good strong flame till the mass is nearly dry—a little pastiness still remaining here and there. It is best to remove the cover when the liquid gets pasty. Allow to cool a minute or two. Take up with hot water and boil a few minutes. Cool by placing in a larger dish of cold water. Pour into a 500 cc. measuring flask. Nearly neu-



tralize with sodium carbonate. Add zinc oxide emulsion until sudden stiffening of the solution. Dilute to the mark. Pour in a dry beaker, mix with rod, and pour through a very large ribbed filter into a 250 cc. measuring flask. When the liquid has reached the mark, withdraw, and transfer to a 500 cc. Erlenmeyer flask. Heat to boiling. Add nearly the full amount of permanganate of strength exactly 0.0055, if the percentage of manganese is approximately known. If not add only one and a half cc. permanganate, and boil until the manganese dioxide separates in flakes, and the liquid becomes yellow. Finish the titration shaking after each addition of permanganate till the yellow reappears. The number of cc. permanganate divided by ten will give the percentage of manganese.

Where the method is in daily use, it will be well to use for neutralizing before adding zinc oxide common sal soda instead of the expensive chemically pure carbonate. But this will add about 0.03 per cent. to the manganese, and must be determined and deducted. The sal soda can be procured at grocery or drug stores. Two pounds in two liters of water (and filtered) is a convenient solution.

The impurity is best determined by doing a steel with pure sodium carbonate, then with the sal soda. For convenience, the amount of the soda solution required to nearly neutralize the manganese solution is noted, and that amount is then at once added in subsequent determinations.

## AN EARLY AMERICAN ARRANGEMENT OF THE ELEMENTS.

BY F. P. VENABLE.

Received September 23, 1895.

IN going over the papers published during the period immediately following the announcement of the Periodic Law, there is one which possesses especial interest for an American.

It is the "Synoptical Tables of the Elements" by Dr. L. R. Gibbes, of Charleston, appearing in the publications of the Elliott Society in 1875. This table had been prepared some two or three years previously for the use of his classes. In it a professor in a remote and small American college worked out for himself, evidently in ignorance of the arrangements of Mende-



ments in an ascending scale of atomic weights, though they are broken up into three series. With much acute reasoning and insight, Gibbs shows that the three series may be exhibited in continuity as one, that is, by the use of an Archimedean Spiral whose radius vector increases by sixteen units in one revolution.

This is the arrangement of Lothar Meyer and de Chancourtois and the spiral suggested by Mendeleeff. His diagram will, on investigation, be seen to be based on the same principles as those of Spring, Reynolds and Crookes.

The author goes further and anticipates some of the geometrical work of Haughton. He observes that no linear equation can be constructed to give more than rude approximations to the atomic weights, and that to construct curves, two points of inflection or contrary curvature must be given. These are the serpentine cubics afterwards worked out by Haughton.

He cautions against laying too much stress upon such arithmetical and geometric exercises.

It seems remarkable that, with so imperfect a table, so much of the later work, done with the perfected tables given by the authors of the Periodic Law, should have been anticipated, especially when we notice how slight was Gibbs' idea of periodicity. He gives in his table seven groups, it is true, four negative and three positive, but they are very poorly filled out, and he shows no completed period of seven in the entire table. His observed regularities can scarcely refer to periodicity, still he makes some mention of what Meyer calls double periodicity, though of course not under this name.

Dr. Gibbs was a professor in the College of Charleston, a fine physicist and a thoughtful chemist. These "Synoptical Tables" which he built up upon the work of Dumas, Gladstone, Cooke, Odling and Barker, speak highly for his insight and power of reasoning.

UNIVERSITY OF NORTH CAROLINA, Sept. 1895.

10-27-95

# ON THE ESTIMATION OF PHOSPHORIC ACID BY TITRATION OF THE AMMONIUM PHOSPHOMOLYBDATE PRECIPITATE WITH STANDARD ALKALI.<sup>1</sup>

By B. W. KILGORE.

Received September 30, 1895.

IN November, 1894, the writer published<sup>2</sup> some results of an investigation of the method on this principle as originally described<sup>3</sup> by Mr. H. Pemberton, Jr., and as modified by the writer, together with an account of some work upon molybdic solutions and temperatures of precipitation best suited for obtaining ammonium phosphomolybdate uncontaminated with molybdic acid.

These investigations were undertaken in part by the writer as reporter of the Association of Official Agricultural Chemists on methods for determining phosphoric acid for 1893-94, to see if the volumetric method was sufficiently accurate and trustworthy, or if it could be developed into a sufficiently reliable method to be used by these chemists in their official work.

The present official gravimetric method is rather long and often gives quite varying results in the hands of different analysts and not always the most concordant ones in the hands of the same analyst. These two objections to the molybdate method, together with the immense volume of phosphoric acid work which has to be done in connection with "Fertilizer Control Stations" and fertilizer factories makes it doubly important that a quick and accurate method for phosphoric acid estimation should, if possible, be found.

The volumetric method seemed to promise well, and it was accordingly sent out, both as originally described by Pemberton and as modified by the writer, to various official and other chemists interested in phosphoric acid work for trial. Three phosphate samples were prepared upon which to conduct the investigations.

No. 1 was a mixture of cottonseed meal and castor pomace, containing about two and a half per cent. phosphorus pentoxide.

No. 2 was an acid phosphate containing about seventeen per cent. phosphorus pentoxide.

<sup>1</sup> This with some additional matter will appear in a bulletin from the North Carolina Experiment Station.

<sup>2</sup> This Journal, 16, 765.

<sup>3</sup> This Journal, 15, 382.

No. 3 was a solution of chemically pure disodium hydrogen phosphate ( $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ), containing 19.826 per cent. phosphorus pentoxide.

The results obtained in this laboratory<sup>1</sup> on these samples by the different methods and presented to the association are shown in Table I.

These results, with a few exceptions, indicate well for the volumetric method, especially the method as described by the writer, there being only one result (20.10 per cent. on sample 3) by this method without the reasonable error of analysis. The larger percentage of the results however on samples 2 and 3 by the method as carried out by Pemberton are high.

The corresponding results on these samples by some sixteen other chemists were not as a whole nearly so encouraging as those presented above, which was likely due to the greater familiarity with the volumetric method in this laboratory.

Then, too, the very large amount of wash water (amounting in some cases to more than a liter) found necessary by a great many to remove free acid from the precipitate made the washing tedious and gave the method little or no advantage in most hands as regards time over the gravimetric method and no advantage in point of accuracy, the latter being especially true when it is made known that now and then unaccountably high results would be obtained by many in the midst of good ones. Notwithstanding these difficulties, most of the chemists who had tried the volumetric method in the different forms in which it was worked up to this time, considered their results on a whole as encouraging, but not such as to give them any considerable faith in the method, especially for high percentages.

At this point the writer again commenced studying further the volumetric method in its various phases and trying numerous modifications to it.

The results obtained last year<sup>2</sup> by the writer's modification of the Pemberton method, consisting of a different molybdc solution and temperature of precipitation, were much more uniform and satisfactory than those obtained by the original Pemberton method on the same samples.

<sup>1</sup> The results of other chemists on these samples will be found in Bul. 43, Div. Chem. U. S. Dept. Agr., page 81.

<sup>2</sup> This Journal, 16, 767.

TABLE I. TOTAL PHOSPHORIC ACID IN ABOVE SAMPLES 1, 2, AND 3.

Analyst.	No. 3.						No. 2.						No. 1.					
	Methods and washings.						Methods and washings.						Methods and washings.					
	Official Gravimetric.	Volumetric as carried out by Femberton.	Washings.	Volumetric as carried out by Kilgore.	Washings.	Washings.	Official Gravimetric.	Volumetric as carried out by Femberton.	Washings.	Volumetric as carried out by Kilgore.	Washings.	Official Gravimetric.	Volumetric as carried out by Femberton.	Washings.	Volumetric as carried out by Kilgore.	Washings.		
W. M. Allen...	Per cent.	Per cent.	cc.	Per cent.	cc.	cc.	Per cent.	Per cent.	cc.	Per cent.	cc.	Per cent.	Per cent.	cc.	Per cent.	cc.		
	.....	.....	.....	.....	.....	.....	17.13	.....	.....	17.15	.....	2.52	.....	.....	2.50	.....		
	.....	.....	.....	.....	.....	.....	17.18	.....	.....	17.00	.....	2.52	.....	.....	2.55	.....		
	.....	.....	.....	.....	.....	.....	17.15	.....	.....	17.10	.....	.....	.....	.....	2.55	.....		
F. B. Carpenter	19.93 <sup>2</sup>	20.00	.....	19.85	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....		
	19.94 <sup>3</sup>	20.15	.....	20.10	.....	.....	17.04	17.10	.....	17.15	.....	2.65	2.58	.....	2.55	.....		
	19.93	.....	.....	.....	.....	.....	17.12	17.15	.....	17.15	.....	2.61	2.63	.....	2.58	.....		
	19.91	.....	.....	.....	.....	.....	17.10	.....	.....	.....	.....	.....	.....	.....	.....	.....		
B. W. Kilgore.	20.06	20.35	650	19.85	500	500	17.17	17.20	500	17.15	450	2.42	.....	.....	2.50	250		
	19.93	20.15	850	19.95	500	500	17.12	17.40	500	17.10	450	.....	.....	.....	2.45	250		
	19.84 <sup>4</sup>	20.15	850	19.90	.....	.....	16.98 <sup>1</sup>	.....	.....	16.97	450	.....	.....	.....	.....	.....		
	19.83 <sup>4</sup>	20.10	1,000	19.90	.....	.....	16.98 <sup>1</sup>	.....	.....	17.00	500	.....	.....	.....	.....	.....		
C. B. Williams.	19.91 <sup>2</sup>	.....	.....	19.80	.....	.....	.....	.....	.....	17.10	500	.....	.....	.....	.....	.....		
	19.85 <sup>3</sup>	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....	.....		
	20.03 <sup>3</sup>	.....	.....	.....	.....	.....	.....	.....	.....	17.10	500	.....	.....	.....	2.50	500		
	20.05 <sup>3</sup>	.....	.....	.....	.....	.....	16.96 <sup>4</sup>	.....	.....	17.10	500	.....	.....	.....	2.50	.....		

<sup>1</sup> The "white" precipitate was dissolved and reprecipitated.<sup>2</sup> Precipitated with magnesia mixture; direct.<sup>4</sup> One gram citric acid added before precipitating with magnesia mixture.

This modified method gave quite as good results in the writer's hands as did the official method. It was therefore decided to use this modified procedure, that is, precipitation at 60° C., and with the official molybdic solution as the starting-point for the investigation.

Knowing that the deposition of molybdic acid was the cause of the trouble in the volumetric method, various ways of getting rid of it were tried. One attempt was to dissolve the ammonium phosphomolybdate in the least possible quantity of concentrated ammonia, thus changing any molybdic acid to ammonium molybdate, acidifying with nitric acid, evaporating to dryness and heating to drive off all nitric acid. This was not practicable for other reasons than that molybdic acid was again formed from the ammonium molybdate on heating to a temperature that would drive off nitric acid. Distillation of the ammonia from the "yellow precipitate" and the calculation of the phosphoric acid from that would not do in that the deposit of molybdic acid carries ammonium molybdate with it. Finally it was determined to try to find wash solutions, which would dissolve molybdic acid, but not ammonium phosphomolybdate.

Using a chemically pure disodium hydrogen phosphate containing 19.826 per cent. phosphorus pentoxide, the following results were obtained with different strengths of nitric acid for washing, finishing with potassium nitrate solution and water to remove nitric acid.

## WASH SOLUTIONS.

No. of times washed with water by decantation.	No. of times washed with dilute nitric acid by decantation.	No. of times washed with three per cent. potassium nitrate by decantation.	Washed on filter with water. cc.	5 cc. 1.42 sp. gr. nitric acid in 100 cc. water.	10 cc. 1.42 sp. gr. nitric acid in 100 cc. water.	20 cc. 1.42 sp. gr. nitric acid in 100 cc. water.	Washed with water only. per cent.
				per cent.	per cent.	per cent.	
.	1	2	275	....	....	19.80	....
1	1	1	275	....	19.84	....	....
2	1	.	275	19.98	....	....	....
.	2	1	400	....	....	19.80	....
.	2	1	400	....	19.87	....	....
1	2	.	275	19.80	....	....	....
3	.	.	400	....	....	....	19.98
.	2	1	230	....	19.87	....	....
.	2	1	350	....	19.83	....	....
3	.	.	700	....	....	....	19.93
3	.	.	550	....	....	....	19.87

The washing with dilute nitric acid and three per cent. potassium nitrate solution was always by decantation, using fifty cc. to seventy-five cc., agitating thoroughly and allowing the precipitate to settle completely each time. When the washing was with water alone, the results are high, while washing twice by decantation with the wash containing ten cc. 1.42 sp. gr. nitric acid in 100 cc., once by decantation with three per cent. potassium nitrate solution, and then with about 300 cc. water on the filter, the results are close to theoretical ones.

*Solubility of Molybdic Acid in Various Wash Solutions.*—It now seems important to investigate the solubility of molybdic acid in various solutions which might be used for washing. The results of this work are contained in the table below and the solubility is expressed in terms of the number of cc. of the standard volumetric alkali neutralized by the molybdic acid dissolved. 100 cc. of this alkali equals 32.38 cc. normal alkali.

SOLUBILITY OF  $\text{MoO}_3$  IN VARIOUS WASH SOLUTIONS.

No. $\text{MoO}_3$ used.	Amount of $\text{MoO}_3$ grams.	Amount of solution cc.	Time of standing, hours.	Water.	2 cc. 1.42 sp. gr. nitric acid in 100 cc. water.	5 cc. 1.42 sp. gr. nitric acid in 100 cc. water.	10 cc. 1.42 sp. gr. nitric acid in 100 cc. water.	20 cc. 1.42 sp. gr. nitric acid in 100 cc. water.	2.5 per cent. potassium nitrate.	5 per cent. potassium nitrate.	5 per cent. sodium nitrate.
1	1	100	1	1.4 <sup>1</sup>	..	..	5.6	6.8	0.4 <sup>2</sup>	0.5 <sup>2</sup>	0.5 <sup>2</sup>
2	1	100	2	..	7.4	8.1	8.8	..	..	7.5 <sub>2</sub>	..
3 {	1	100	1	..	..	..	2.8 <sup>3</sup>	..	3% $\text{KNO}_3$	..	..
	1	100	1/2	..	1.3 <sup>2</sup>	1.5	2.0, 2.3	2.8	0.92	..	..
	1	100	1	0.45 <sup>2</sup>	0.8	1.5	2.5	3.1	2.5	..	..
4 {	1	100	1/2	..	2.4 <sup>2</sup>	3.55 <sup>2</sup>	5.15	6.3	0.92 <sup>2</sup>	..	..
	1	100	1	..	2.9 <sup>2</sup>	4.7 <sup>2</sup>	7.3	8.85	1.0 <sup>2</sup>	..	..
5 {	1	100	1/2	..	..	..	2.2	..	0.8	..	..
	1	100	1	1.4 <sup>4</sup>	..	..	2.2	..	0.7	..	..
	1	100	1	..	..	..	2.8	..	0.8	..	..
	1	100	1	..	..	..	2.8	..	0.8	..	..

<sup>1</sup> Stood eighteen hours and then filtered turbid, though double filter was used; result too high.

<sup>2</sup> Filtered turbid; results too high.

<sup>3</sup> Used as in washing the yellow precipitate. One portion of 100 cc. was added, stirred and allowed to stand fifteen minutes, and filtered off; then another 100 cc. portion was added and titrated in the same way.

<sup>4</sup> Stood twenty-four hours before a clear filtrate could be obtained.



These solubility determinations were made by allowing 100 cc. of the respective solutions to stand in a beaker with the molybdic acid for the time indicated in the table, stirring once or twice to keep the molybdic acid in contact with the liquid, but allowing sufficient time before filtration for most of it to settle to the bottom of the beaker. The washes were then filtered through double filters, evaporated to dryness (when nitric acid was present), heated in an air-bath until nitric acid was driven off, and titrated. It was found very difficult to prevent the molybdic acid from passing through the filter when water was used as the solvent. It would remain suspended in a very finely divided state in water for twenty-four hours and pass through the filter. The results for the water solubility are therefore generally too high. This is also true to a less extent of the solubility in two and a half, three, and five per cent. potassium nitrate solutions, and in the five per cent. sodium nitrate solution; and to a still less extent of the solubility in two and five cc. nitric acid solutions.

The results are not all uniform but fairly so when the same molybdic acid was used. None of these molybdic acids were pure.

Numbers 1 and 2 contained considerable quantities of ammonium nitrate and ammonium molybdate, and perhaps some sodium molybdate. Numbers 3, 4, and 5 were washed by decantation for a day or more with large quantities of dilute nitric acid, and finally once or twice with water, and contained, so far as we ascertained, only ammonium molybdate as impurity. The impurities did not, we think, materially affect the solubility of these acids in the wash solutions. The results, at any rate, are of value in showing the comparative solvent action of the different washes for molybdic acid under conditions similar to those in which they are used in the method.

They show that water, and sodium and potassium nitrate solutions have very little solvent action upon molybdic acid; while that of the stronger nitric acid solutions is quite considerable. After all, these results may represent more nearly what we want than they would, had pure molybdic acid been

used ; for in the volumetric method it is not a solvent for molybdic acid alone that is wanted, but for a mixture of molybdic acid and ammonium molybdate perhaps in quite variable quantities.

Of the dilute nitric acid washes, the one containing ten cc., 1.42 sp. gr., nitric acid in 100 cc. of the wash was adopted because it possesses good solvent power for molybdic acid and is of practically the same acidity as the solution in which the precipitation of ammonium phosphomolybdate is made in the official method. The official molybdic solution contains nearly fifteen cc., 1.42 sp. gr., nitric acid in fifty cc. ; and a solution requiring fifty cc. of molybdic solution to precipitate the phosphoric acid in it usually has a volume near 100 cc. ; the two would give a volume of 150 cc, containing about ten cc. nitric acid in the 100 cc.

We know that precipitation is complete in a solution of this acidity, and no solvent action takes place on long standing. It therefore seems reasonable to conclude that nitric acid of the same strength would exert little or no solvent action on the ammonium phosphomolybdate in the short time required to wash the precipitate.

#### SOLUBILITY OF AMMONIUM PHOSPHOMOLYBDATE IN THE FOREGOING WASH SOLUTIONS.

It now appeared desirable to investigate the solubility of ammonium phosphomolybdate in these same wash solutions. This was done by preparing a pure phosphomolybdate from sodium phosphate by precipitating with a deficient quantity of molybdic solution, pouring off the filtrate, washing by decantation with dilute nitric acid, and finally with water to remove most of the nitric acid, and drying to constant weight at 130° to 150° C. This phosphomolybdate contained 3.789 per cent. phosphorus pentoxide, the theory being 3.783, showing that it was practically pure. The solubility is expressed in terms of the number of cc. of standard volumetric alkali required to neutralize the phosphomolybdate dissolved. One cc. of this alkali equals one milligram phosphorus pentoxide.

## SOLUBILITY OF AMMONIUM PHOSPHOMOLYBDATE IN WASH SOLUTIONS.

	Amount of solution.		Time of standing—hours.	Water at 65° C.	Water at laboratory temperature, about 27° C.	2 cc. HNO <sub>3</sub> in 100 cc. wash.	5 cc. HNO <sub>3</sub> in 100 cc. wash.	10 cc. HNO <sub>3</sub> in 100 cc. wash at 65° C.	10 cc. HNO <sub>3</sub> in 100 cc. wash at laboratory temperature.	20 cc. HNO <sub>3</sub> in 100 cc. wash.	3 per cent. KNO <sub>3</sub> solution.
0.75 to 1.4 grams substance stood in 500 cc. of the solution for the time indicated, and 200 cc. was taken each time for the test.	200	24		5.2 <sup>1</sup>	0.85 <sup>1</sup>	0.2	0.25	20.1	0.6	0.75	0.5
	200	106		6.0 <sup>2</sup>	3.0 <sup>2</sup>	2.05	5.5	16.75 <sup>3</sup>	6.75	11.45	4.35
Results from allowing precipitates from 20 per cent. phosphate to stand in these solutions.	200	$\frac{1}{2}$		..	none	..	none	..	none	none	none
	200	1		..	trace	..	trace	..	trace	trace	trace

From 0.75 to one and four-tenths grams of the prepared phosphomolybdate was shaken up in flasks with 500 cc. of the wash solutions. Two hundred cc. of this was filtered off at the end of twenty-four hours and 106 hours respectively, evaporated to dryness (when nitric acid was present), the nitric acid driven off, and the residue titrated. The phosphomolybdate settled in only two or three of these washes in less time than twenty-four hours, and even then the very fine particles remained suspended in the water solutions, and it was found impossible to get clear filtrates from them. The results for water-solubility are therefore too high. For the reason just stated the solubility of ammonium phosphomolybdate in the washes could not be determined for the times they would ordinarily stand in contact with the precipitate in washing by the use of the pure molybdate. If, however, the solubility of even this pure phosphomolybdate was proportional to the time of standing in the washes, the amount that would have been dissolved by all the washes (dilute nitric acid, potassium nitrate, and water) used in washing a precipitate in the ordinary thirty minutes required for washing could hardly have been found. I calculated that on this basis a plus correction of

<sup>1</sup> These filtered very turbid; they had not settled in twenty-four hours.

<sup>2</sup> These stood at laboratory temperature (about 27° C.) after first twenty-four hours.

<sup>3</sup> Filtered turbid; results too high.

about 0.016 per cent. would be necessary on basis of two-tenths gram substance.

The solubility of the "yellow precipitate" just as it is precipitated in ordinary work along with the salts carried down with it was also determined in the wash solution by allowing 200 cc. of them to stand in contact with the precipitate for one-half and one hour, respectively, after stirring thoroughly. The precipitates settled completely and quickly in this way. In none of these washes could more than a trace of phosphoric acid be found. Again all the washings (3600 cc.) from six determinations of phosphoric acid in two phosphate solutions (a 3.30 per cent. and a 19.83 per cent.) were combined, evaporated down and the phosphoric acid in them determined by the gravimetric method, when 0.38 milligrams phosphorus pentoxide was found, corresponding to a plus correction of 0.03 per cent. on basis of two-tenths gram substance. A similar result was obtained from the washings from eight determinations on the same samples.

These results indicate that while the wash solutions used in the volumetric method have marked solvent power for molybdic acid, they have practically no solvent action on ammonium phosphomolybdate, and that a correction for ordinary work at least is not necessary. There is danger, however, of mechanical loss. The precipitate is first washed by decantation with dilute nitric acid and potassium nitrate, and afterwards with water to remove nitric acid. In this after washing, when all the salts have been removed from the precipitate and as much as 600 or 700 cc. has been used, the precipitate begins to pass through the filter mechanically and settle to the bottom of the receptacle. We have not, however, found it necessary to wash with more than 300 cc. of water in our present manipulation of the method. We consider that 500 or 600 cc. of water may be used without this loss, but the filtrate should be closely observed when the washing goes beyond this amount.

#### INVESTIGATION OF MOLYBDIC SOLUTIONS.

Besides the comparison of the aqueous molybdate of Pemberton with the official molybdic solution recorded in my last year's work,<sup>1</sup> nine other molybdic solutions of different formulas, in-

<sup>1</sup> This Journal, 16, 769.

cluding five or six of those most highly recommended by different analysts, and the remainder of our own making, have been tried. The formulas of these solutions need not be given. They varied quite widely in the proportions of molybdic acid to free nitric acid and ammonium nitrate as well as in degrees of concentration.

Without going into a detailed discussion of the results and the advantages possessed by the different molybdic solutions for different purposes, we will merely state that we found the official molybdic solution of the following formula and made by dissolving 100 grams of molybdic acid in 400 grams, or 417 cc., of ammonia of 0.96 sp. gr., and pouring this into 1250 cc., or 1500 grams nitric acid of 1.20 sp. gr. to be the one best suited to the volumetric method for very small quantities of phosphoric acid, one per cent or less. For percentages larger than one, the foregoing solution with the addition of eighty extra cc. of 1.42 sp. gr. nitric acid, or five cc. to each 100 cc. of official molybdic solution was found to be the best. 100 cc. of this latter solution contains practically six grams of molybdic acid, four and six-tenths grams ammonium nitrate, and thirty-five cc. free nitric acid of 1.42 sp. gr., which is about the largest quantity of free nitric acid in proportion to molybdic acid that can be used in a molybdic solution not to interfere with quick and ready precipitation of phosphoric acid. When a larger proportion of free nitric acid is in the solution, precipitation of phosphoric acid is either incomplete or is very materially retarded. This modified official molybdic solution, containing the large amount of nitric acid, can be readily used for all percentages of phosphoric acid, but it contains rather too much free nitric acid to allow of the quickest precipitation of very small quantities, but by extending the time of precipitation to eight to ten minutes it will be found to be complete even when very small amounts are present. The judgment and manipulation of the analyst will, however, be the best guide as to whether he will employ the solution containing the larger amount of nitric acid for all percentages, or whether he will only use it for those above one or so, and use the regular official solution for less amounts.

EFFECT OF ORGANIC ACIDS IN PREVENTING DEPOSITION OF  
MOLYBDIC ACID.

Jüptner<sup>1</sup> has successfully used two-tenths to six grams of tartaric acid per 100 cc. of molybdic solution for preventing the deposition of molybdic acid in the determination of phosphorus in steel. One to four grams of citric acid to 100 cc. of the two foregoing molybdic solutions were employed in the hope of accomplishing the same object. When three and four grams of citric acid were used precipitation was not complete in fifteen or twenty minutes, and with smaller quantities (one, one and five-tenths, and two grams) precipitation was complete in a reasonable length of time (seven to fifteen minutes), but the results at best showed no advantage over those obtained on the same samples with molybdic solutions without the presence of citric acid.

## ACIDITY OF AMMONIUM PHOSPHOMOLYBDATE.

Hundeshagen<sup>2</sup> has stated that it required twenty-three molecules of  $\text{Na}_2\text{CO}_3$  (or of  $\text{Na}_2\text{O}$ ) to neutralize the ammonium phosphomolybdate containing one molecule of phosphorus pentoxide.

H. Pemberton, Jr.,<sup>3</sup> working upon a solution of chemically pure disodium hydrogen phosphate, found that 23.2 molecules of sodium carbonate were necessary to neutralize the ammonium phosphomolybdate containing one phosphorus pentoxide molecule; a second determination,<sup>4</sup> however, working in the same way, gave him 22.99 molecules.

In the course of my work upon the volumetric method, I have determined the acidity of ammonium phosphomolybdate in two ways. First, by finding the amount of alkali necessary to neutralize the ammonium phosphomolybdate formed from a given amount of phosphate. This was done by dissolving ten grams of chemically pure disodium hydrogen phosphate in a liter of water, carefully measuring out twenty cc. portions, precipitating with molybdic solution, washing thoroughly according to our practice in the volumetric method, and titrating with alkali.

The results obtained are as follows :

<sup>1</sup> Abs. Expt. Sta. Record, 6, 610.

<sup>2</sup> *Ztschr. anal. Chem.*, 28, 141-172.

<sup>3</sup> *This Journal*, 15, 382.

<sup>4</sup> *Ibid*, 16, 278.

	Cc. of phosphate solution used.	Equaling grams $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ .	Equaling grams $\text{P}_2\text{O}_5$ .	Cc. KOH solution required to neutralize phosphomolybdate formed.
1	20	0.20000	0.039652	39.80
2	20	0.20000	0.039652	39.80
3	20	0.20000	0.039652	39.80

Dividing the weight of phosphorus pentoxide by the number of cc. alkali required to neutralize the phosphomolybdate formed, we find that 100 cc. alkali has neutralized an amount of ammonium phosphomolybdate containing 99.628 milligrams phosphorus pentoxide.

The alkali was now titrated against semi-normal hydrochloric acid, carefully standardized by silver nitrate to contain 18.2285 grams hydrochloric acid per liter. 100 cc. of the alkali equaled 64.5 cc. of the semi-normal acid, which contained 1175.74 milligrams hydrochloric acid, which in turn equals 1519.3 milligrams potash, or 2228.6 milligrams potassium carbonate. Therefore, 1519.3 milligrams potash equals 99.628 milligrams phosphorus pentoxide in the yellow precipitate. Dividing each of these by its molecular weight, we obtain

$$\text{for phosphorus pentoxide } \frac{99.628}{142.06} = 0.7013.$$

$$\text{for potash } \frac{1519.3}{94.22} = 16.125.$$

$$\text{Then, } \text{P}_2\text{O}_5 : \text{K}_2\text{O} = 0.7013 : 16.125 = 1 : 22.993.$$

The relation between standard alkali and phosphorus pentoxide in the "yellow precipitate" was now determined by preparing pure phosphomolybdates by precipitating sodium phosphate with a deficient quantity of molybdic solution, pouring off the filtrate, washing by decantation, first with dilute nitric acid and then with water, and drying at 130° to 150° C. to constant weight. These phosphomolybdates contained 2.232 per cent. nitrogen (average of seven analyses), the theory being 2.238; and 1.645 per cent. phosphorus, the theory being 1.651. The following results were obtained by titrating a portion of three of these :

	Grams ammonium phosphomolybdate used.	Cc. standard alkali required to neutralize.
1	1.2322	46.55
2	0.8050	30.45
3	0.7955	30.10
Total	2.8327	107.10

One hundred cc. of alkali has, therefore, neutralized 2.6449 grams of ammonium phosphomolybdate, which multiplied by 3.783, (the per cent. of phosphorus pentoxide in the "yellow precipitate") gives 100.05 milligrams phosphorus pentoxide in 2.6449 grams of this salt, and which corresponds to 100 cc. of the alkali used.

One hundred cc. of this alkali was found as before to equal 64.74 cc. semi-normal hydrochloric acid, which contains 1180.14 milligrams hydrochloric acid, and which in turn equals 2237.08 milligrams of potassium carbonate. Therefore 2237.08 milligrams potassium carbonate equals the 100.05 milligrams of phosphorus pentoxide contained in the 2.6449 grams of "yellow precipitate."

Dividing by molecular weights, there is found

$$\text{for phosphorus pentoxide } \frac{100.05}{142.06} = 0.7042.$$

$$\text{for potassium carbonate } \frac{2237.08}{138.22} = 16.185.$$

$$\text{Therefore, } P_2O_5 : K_2CO_3 = 0.7042 : 16.185 = 1 : 22.983.$$

It has, therefore, required practically twenty-three molecules of potassium carbonate (or of potash) to neutralize an amount of ammonium phosphomolybdate ( $6NH_4.P_2O_5.24MoO_3$ ) containing one molecule of phosphorus pentoxide. On this basis, one cc. of a standard alkali containing 18.17106 grams of potassium hydroxide to the liter would equal one milligram phosphorus pentoxide. 100 cc. of this solution will neutralize 32.38 cc. of normal acid; and either the acid or alkali to be used in the volumetric method can be made by diluting 323.8 cc. of corresponding normal solution to one liter.

The above calculations are based upon the following atomic weights:

Sodium.....23.05	Oxygen.....16.	Chlorine.....35.45
Hydrogen ... 1.007	Potassium ...39.11	Molybdenum 96.
Phosphorus..31.03	Carbon .....12.	Nitrogen ....14.03

#### RESULTS BY VOLUMETRIC METHOD AS NOW WORKED IN THIS LABORATORY COMPARED WITH GRAVIMETRIC RESULTS.

The writer was again reporter of the Association of Official Agricultural Chemists on methods for determining phosphoric acid for 1894-95, and the foregoing investigation was made with a view of setting the method in better shape for trial by this



association and for perfecting it, if possible, for use in this laboratory. The method was accordingly changed quite materially, redescribed to accord with results of the preceding work, and sent out to various official and other chemists for trial with three samples upon which to conduct the work. These samples were :

No. 1 was a chemically pure disodium hydrogen phosphate solution containing ten grams of the salt per liter, the theoretical percentage of phosphorus pentoxide in it being 19.826.

No. 2 was solution No. 1 diluted with five parts of water, and therefore contained the equivalent of 3.304 per cent. phosphorus pentoxide in fifty cc.

No. 3 was a mixed fertilizer.

The results obtained in this laboratory on these samples by gravimetric and volumetric methods and presented to the association are brought together in Table II.

These results are what, I deem, may be termed *most excellent*.

It may not be out of place here to state also that the results of nine other chemists on these same samples, including thirty-one determinations on No. 1 and thirty-three on No. 2, excluding three results, are as good as those in the table. Seventy-three per cent. of all the results of thirteen chemists on sample No. 1 are within 0.05 per cent. of the theory, and ninety-three per cent. within one-tenth per cent., there being only three results varying more than one-tenth. On sample No. 2 eighty-five per cent. of all results are within 0.05 per cent. of the theory and all are within one-tenth.

This summary of results of members of the Association of Official Agricultural Chemists by the volumetric method are in rather marked contrast to the results of this and all previous years by the official gravimetric method, and also to the results by the volumetric method as worked last year. The results last year by the volumetric method were considered on the whole as encouraging, while the method as worked this year has given extremely good results in all hands.

The volumetric and gravimetric methods have been compared in this laboratory upon quite a variety of phosphates and fertilizer materials of varying percentages. The results follow in Table III.

TABLE II. TOTAL PHOSPHORIC ACID BY GRAVIMETRIC AND VOLUMETRIC METHODS.

Analyst.	Sample No. 1.					Sample No. 2.					Sample No. 3.				
	Methods and washings.					Methods and washings.					Methods and washings.				
	Official Gravimetric.	Volumetric.	Washing water.	Difference + than gravimetric.	Per cent.	Official Gravimetric.	Volumetric.	Washing water.	Difference + than gravimetric.	Per cent.	Official Gravimetric.	Volumetric.	Washing water.	Difference + than gravimetric.	Per cent.
W. M. Allen	19.93	19.81	275			3.38	3.28	265			12.50	12.32	275		
	19.97	19.84	250	-.11		3.39	3.27	300			12.59	12.39	300		
	19.96	19.88	285				3.27	275				12.39	350		-17
							3.29	275	-109						
C. B. Williams							3.28	300							
							3.27	275							
	19.91	19.80	220				3.32	210				12.32	240		
		19.85	230				3.32	220				12.32	270		
F. B. Carpenter		19.85	250				3.32	205				12.32	235		
		19.85	250				3.32	220				12.42	220		
	19.83	19.85	275			3.38	3.32	250			12.43	12.39	250		
		19.87	275			3.33	3.34	250			12.37	12.43	250		
B. W. Kilgore.	19.96	19.83	280			3.38	3.32	300				12.40	225		
	19.89	19.83	280			3.39	3.31	200				12.40	190		
	20.00	19.83	250			3.40	3.30	200				12.37	200		
							3.30	210				12.37	250		
Average.....	19.93	19.84				3.38	3.302				12.475	12.37			
Theory.....	19.826	19.826				3.304	3.304								
Variation of lowest result from theory.....	0.004	0.026				0.026	0.034								
Variation of highest result from theory.....	0.174	0.054				0.096	0.034								

## PHOSPHORIC ACID.

TABLE III. DETERMINATIONS OF PHOSPHORIC ACID IN VARIOUS MATERIALS BY VOLUMETRIC AND GRAVIMETRIC METHODS.

Material.	Number.	Gravimetric Method.	Volumetric method.	Washing water.	Difference greater + less than gravimetric method.	Material.	Number.	Gravimetric method.	Volumetric method.	Washing water.	Difference greater + less than gravimetric method.
C. B. Williams, Analyst.....											
Cottonseed meal	1	0.08	0.08	130	.00		16	9.54	9.45	260	-.09
	2	0.37	0.35	100	-.02		17	10.72	10.65	270	+.07
	3	1.32	1.28	100	-.04		18	6.46	6.40	230	-.06
	4	1.50	1.45	215	-.05		19	6.55	6.60	250	+.05
	5	0.88	0.79	215	-.09		20	5.45	5.50	290	+.05
	6	0.05	0.01	230	-.04		21	6.32	6.60	280	+.08
	7	0.04	0.01	230	-.03	Fertilizers and fertilizing materials	22	7.47	7.44	250	+.03
	8	1.27	1.25	240	-.02		23	7.42	7.44	230	+.04
	9	1.29	1.25	230	-.04		24	17.55	17.52	260	-.03
	10	4.96	4.95	185	-.01		25	17.35	17.32	260	-.03
	11	4.98	4.92	180	-.06		26	38.12	37.80	260	-.30
	12	11.80	11.80	120	.00	Florida phosphate	27	15.49	15.35	280	-.14
	13	11.58	11.45	230	-.13	Acid phosphate	28	13.57	13.15	260	-.42
	14	9.77	9.80	240	+.01						
	15	10.04	10.05	220							
W. M. Allen, Analyst.....											
Mixed fertilizer	1	11.58	{ 11.45 11.48 11.53 9.50 9.53	{ 250 260 280 275 285	-.09	Acid phosphate	3	15.49	{ 15.47 15.43 10.70 15.35	{ 250 275 260 275	-.04
"	2	9.54	{ 9.50 9.53	275	-.02	Mixed fertilizer	4	10.72	{ 10.67 10.67 15.35	275	-.03
B. W. Kilgore, Analyst.....											
Mixed fertilizer	1	9.77	9.76	275	.00	Mixed fertilizer	11	10.72	10.68	275	-.04
"	2	9.75	8.96	210	-.07	Acid phosphate	12	13.27	13.21	275	-.06
"	3	9.03	10.66	220	+.02	Mixed fertilizer	13	11.71	11.63	275	-.08
"	4	11.58	11.60	275	+.01	"	14	11.88	11.75	275	-.13
"	5	9.77	9.76	275	-.01	"	15	9.43	9.38	250	-.05
"	6	10.04	10.01	275	-.03	Bone meal	16	9.71	9.80	230	+.09
"	7	9.54	9.48	275	-.06	Acid phosphate	17	10.35	10.30	250	-.05
Acid phosphate	8	15.49	15.42	275	+.07	"	18	20.53	20.48	210	-.05
Insoluble	9	2.57	2.60	230	+.03	"	19	15.02	15.10	220	+.08
Reporter's sample No. 1	10	{ 19.96 19.89	{ 19.88 19.88	{ 260 260	-.05	Reporter's sample No. 2	20	{ 3.38 3.39	{ 3.30 3.31	{ 220 220	-.08
Reporter's sample No. 3	21							{ 12.43 12.45	{ 12.43 12.45	{ 260 260	

1C. P.  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O} = 19.86$  per cent.  $\text{P}_2\text{O}_5$ .

These volumetric results show close agreement with the gravimetric ones, though they are generally slightly lower than the latter. When we observe the close agreement of duplicate results by the volumetric method and remember the tendency of the molybdate method to give high results, we have ground for believing that the volumetric results are more nearly correct.

#### RESULTS ON A HIGH GRADE PHOSPHATE.

To see how the volumetric method would work on a very high percentage phosphate and to see how the results by the two methods would compare on it, a high grade Florida phosphate was submitted to analysis, with the following results :

	C. B. Williams, analyst. per cent.	B. W. Kilgore, analyst. per cent.
Gravimetric method.....	38.12	
Volumetric method .....	37.80 37.84	37.80 37.88
Less by volumetric method.....	0.30	

The foregoing results by the volumetric method, our work upon it, and experience with it generally lead us to consider it a more accurate and reliable method than the molybdate-magnesia method. Since the change of temperature of precipitation, precipitating reagent, wash solutions, and manner of washing from what they were in the Pemberton method, the difficulty of getting occasionally very high results in the midst of good ones, and which did so much to destroy faith in the method, seems not to occur under the new method of procedure. The accuracy, reliability and rapidity of the method, a man being able to make, we think, twice as many determinations by it as by the gravimetric method, causes us to feel that the large amount of time which we have put upon the method has been well spent and will soon repay us in the saving of time on this class of work in our own laboratory, to say nothing of the service it may be to others having, as we do, large amounts of phosphoric acid work to do.

I am indebted to Messrs. C. B. Williams and W. M. Allen for assistance in carrying out the foregoing work.

The method, as we have found it to give the best results, may be described as follows :

Weigh two grams of substance and make solution by one of the following methods: (1) Evaporate with five cc. of magnesium nitrate solution, ignite, and dissolve in hydrochloric acid. This is for organic materials. (2) Dissolve in thirty cc. concentrated nitric acid with a small quantity of hydrochloric acid. (3) Add thirty cc. concentrated hydrochloric acid, heat, and add cautiously in small quantities at a time about five-tenths gram of finely pulverized potassium chlorate. These (2. and 3) are for ordinary phosphates and fertilizers. (4) Dissolve in fifteen to thirty cc. of strong hydrochloric acid and five to ten cc. of nitric. This is for phosphates containing much iron and aluminum. Method 2 is preferred when these acids are a suitable solvent for the material. Make up to 200 cc. (or any other convenient volume), measure out twenty cc. for totals, or for percentages above five or six; and forty cc. for insolubles, or for percentages below five or six, corresponding to two-tenths and four-tenths gram substance respectively, add about five cc. concentrated nitric acid, when method 2 for solution has been used and about ten cc. when method 1, 3, or 4 has been used. Now add ammonia until precipitate just begins to form, dilute high percentage solutions to about 100 cc., and low percentage ones to from sixty to seventy-five cc., digest in water-bath at 60° to 65° C., and after filtering the molybdic solution to be used in this method, precipitate, not using any greater excess of molybdic solution than is necessary to insure complete precipitation; let stand in bath six minutes from the time the molybdate is added, and filter as quickly as possible upon a three-inch Hirsch funnel, whose perforations are covered with a disk of soft filter-paper, or in a Gooch crucible with one or two pieces of filter-paper slightly larger than the bottom of the crucible, tightly pressed against the bottom of the crucible, or upon a filter made by putting a platinum cone or disk, well filled with holes, into a three-inch funnel and covering with coarse asbestos, using the pump in all cases. Filter-paper may be used, but the other filters in the order named are much to be preferred.

It is *especially urged* that the three-inch Hirsch funnel be used where possible, as it permits of rapid filtration and easy and thorough washing. Wash the precipitate twice by decantation

with dilute nitric acid, using fifty to seventy-five cc. each time and agitating thoroughly, once by decantation with the same amount of three per cent. potassium or ammonium nitrate solution, then on the filter and with 200 to 500 cc. water, (250 cc. is usually enough) or until no longer acid. Now wash the precipitate with filter back into the beaker, titrate with potassium hydroxide, and back with nitric acid, using phenolphthalein as indicator and adding acid until color disappears.

In washing by decantation, if the precipitate is allowed to settle completely each time, no trouble will be experienced in the after washing.

Where the phosphoric acid is below one per cent., the precipitation is not so rapid as in larger percentages and may require eight or even ten minutes to be complete.

#### REAGENTS TO BE USED IN THE VOLUMETRIC METHOD.

*Molybdic Solution.*—Dissolve 100 grams of molybdic acid in 400 grams, or 417 cc. of ammonia, sp. gr. 0.96, and pour the solution thus obtained into 1500 grams, or 1250 cc. of nitric acid, sp. gr. 1.20, and add eighty cc. nitric acid, sp. gr. 1.42. Or to each 100 cc. of the official molybdic solution (the above formula without the eighty cc. nitric acid), add five cc. 1.42 sp. gr. nitric acid. This solution should be filtered each time before using.

*Dilute Nitric Acid Wash.*—Dilute 100 cc. 1.42 sp. gr. nitric acid to one liter.

*Potassium or Ammonium Nitrate Wash.*—Dissolve three grams of either in 100 cc. of water.

*Alcoholic Solution of Phenolphthalein.*—100 cc. to one gram.

*Standard Potassium Hydroxide.*—This solution should contain 18.17106 grams potassium hydroxide to the liter. One cc. of this solution equals one milligram phosphorus pentoxide (one per cent. phosphorus pentoxide on basis of one-tenth gram substance) 100 cc. of it will neutralize 32.38 cc. normal acid, and can be made by diluting 323.81 cc. of normal potassium hydroxide, which has been freed from carbonates by barium hydroxide to one liter.

*Standard Nitric Acid* of same, or one-half, the strength of alkali. Hydrochloric or sulphuric acid will do.

# THE RELATIONSHIP OF THE HEAT OF VAPORIZATION OF GASES TO THEIR DENSITY AND ALSO TO THEIR BOILING-POINT.

BY WM. L. DUDLEY.

Received September 27, 1895.

IN studying the heat of vaporization or latent heat of various gases it soon became apparent that this constant bore an interesting relationship to their density and boiling-point. To trace out this relationship I have endeavored to obtain the latest and best latent heat determinations, as well as the specific gravity of the liquids at the boiling-point. Accurate data of this kind are scarce, and there are few homologous series in which these constants have been determined for many members. However, I have obtained a sufficient number of trustworthy determinations to show some results, which seem to be worth recording.

The amount of heat absorbed by one cc. of vapor (reduced to 0° and 760 mm. pressure) in the passage of the liquid to the gaseous state, is taken as the standard for comparison. This constant is found by the formula

$$L = \frac{H \times w}{W}.$$

where  $L$  = the heat of vaporization in one cc. of vapor,

$W$  = the weight of one cc. of the liquid at its boiling-point,

$H$  = the heat of vaporization,

and  $w$  = the weight of one cc. of the vapor at 0° and 760 mm. pressure.

Until the latent heat researches made by R. Schiff<sup>1</sup> these constants were determined without any special reference to the relationship of the compounds to one another, and, therefore, not many series can be found complete enough to make a comparison. I believe, however, that I have gathered the data quite completely and I give in this paper all the series in which the data are complete for as many as three members.

In the following tables the columns marked

<sup>1</sup> *Ann. Chem.* (Liebig), 234, 338, 1886.

D = the vapor density,

B. P. = Boiling-point in absolute temperature,

S. G. = Specific gravity at the boiling-point,

H. V. = Heat of vaporization in calories,

V = Volume of vapor, in cubic centimeters (reduced to 0° and 760 mm. pressure), produced from one cc. of liquid at the boiling-point.

L = Heat of vaporization in a unit of volume (one cc.) of gas reduced to 0° and 760 mm. pressure.

The specific gravity of liquids at the boiling-point is taken from Clarke's tables of "Constants of Nature," where the references are fully given. The boiling-point is obtained from Carnelley's tables.

I will first show the results obtained from some of the fatty acids and their alkyl compounds.

Name.	Formula.	FORMATES.					
		D.	B. P.	S. G.	H. V.	V.	L.
Formic acid	HCHO <sub>2</sub>	23	373.8°	1.1175	120.72 <sup>1</sup>	542.26	0.2226
Methyl formate	CH <sub>3</sub> CHO <sub>2</sub>	30	305.3°	0.95196	117.10 <sup>2</sup> 102.70 <sup>3</sup>	354.15	0.3306 0.2900
Ethyl formate	C <sub>2</sub> H <sub>5</sub> CHO <sub>2</sub>	37	326.5°	0.86667	92.15 <sup>4</sup>	263.36	0.3499
Propyl formate	C <sub>3</sub> H <sub>7</sub> CHO <sub>2</sub>	44	354.2°	0.82146	85.25 <sup>4</sup>	208.37	0.4091
Isobutyl formate	C <sub>4</sub> H <sub>9</sub> CHO <sub>2</sub>	51	371.0°	0.7784	77.0 <sup>4</sup>	170.34	0.4520
Isoamyl formate	C <sub>5</sub> H <sub>11</sub> CHO <sub>2</sub>	58	397.0°	0.7554	71.65 <sup>4</sup>	145.35	0.4929

Fig. 1 represents the curves of the formates, the density and boiling-point curves being shown on the same sheet. In all cases the corresponding acids fall in line in the density curves but not in the boiling-point curves. The acids, however, form both density and boiling-point curves of their own, as will be shown later on.

It will be seen from Fig. 1 that the heat of vaporization per unit of volume (H. V.) of methyl formate obtained from the result of Andrews' determination is too high. To conform to the curve it should be 0.2900 which would give 102.70 as the heat of vaporization (H. V.) instead of 117.10 as given by Andrews, whose determination has never been verified. But

<sup>1</sup> Favre and Silbermann : *Ann. chim. phys.* [3], 37, 464-470.

<sup>2</sup> Andrews : *Chem. Soc. Quar. J.*, 1, 27.

<sup>3</sup> Calculated from the data furnished by the curves shown in this paper.

<sup>4</sup> Schiff : *Ann. Chem.* (Liebig), 234, 338.



# HEAT OF VAPORIZATION.

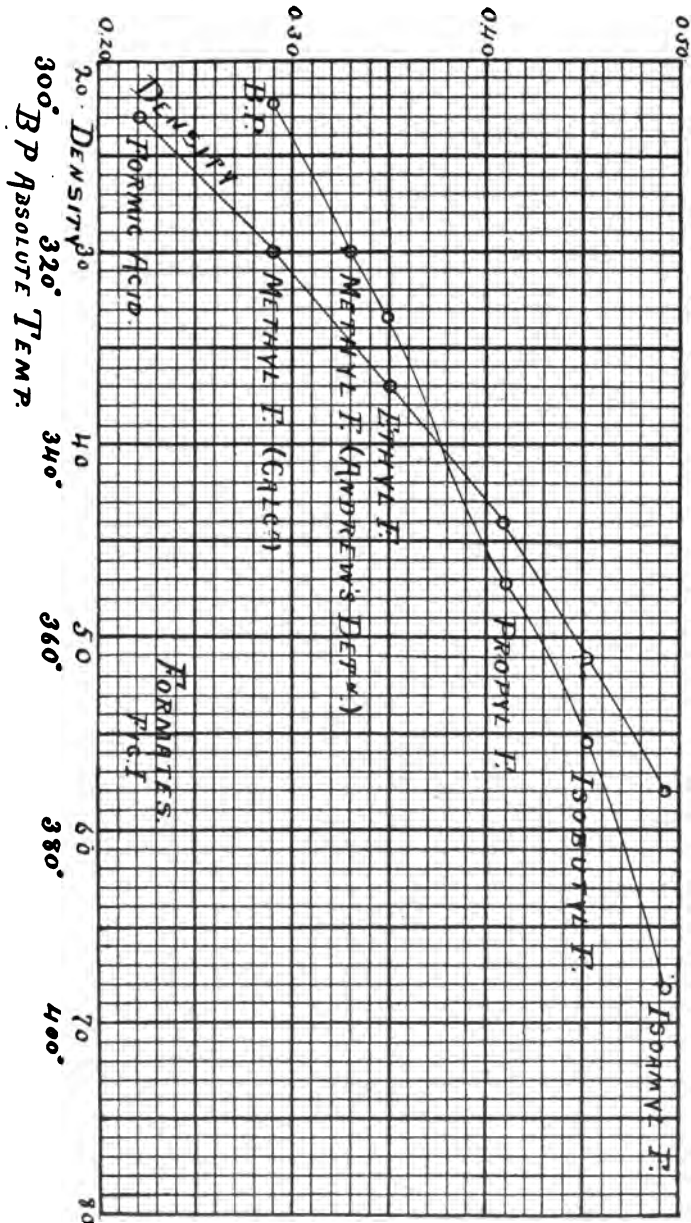


FIG. 1.

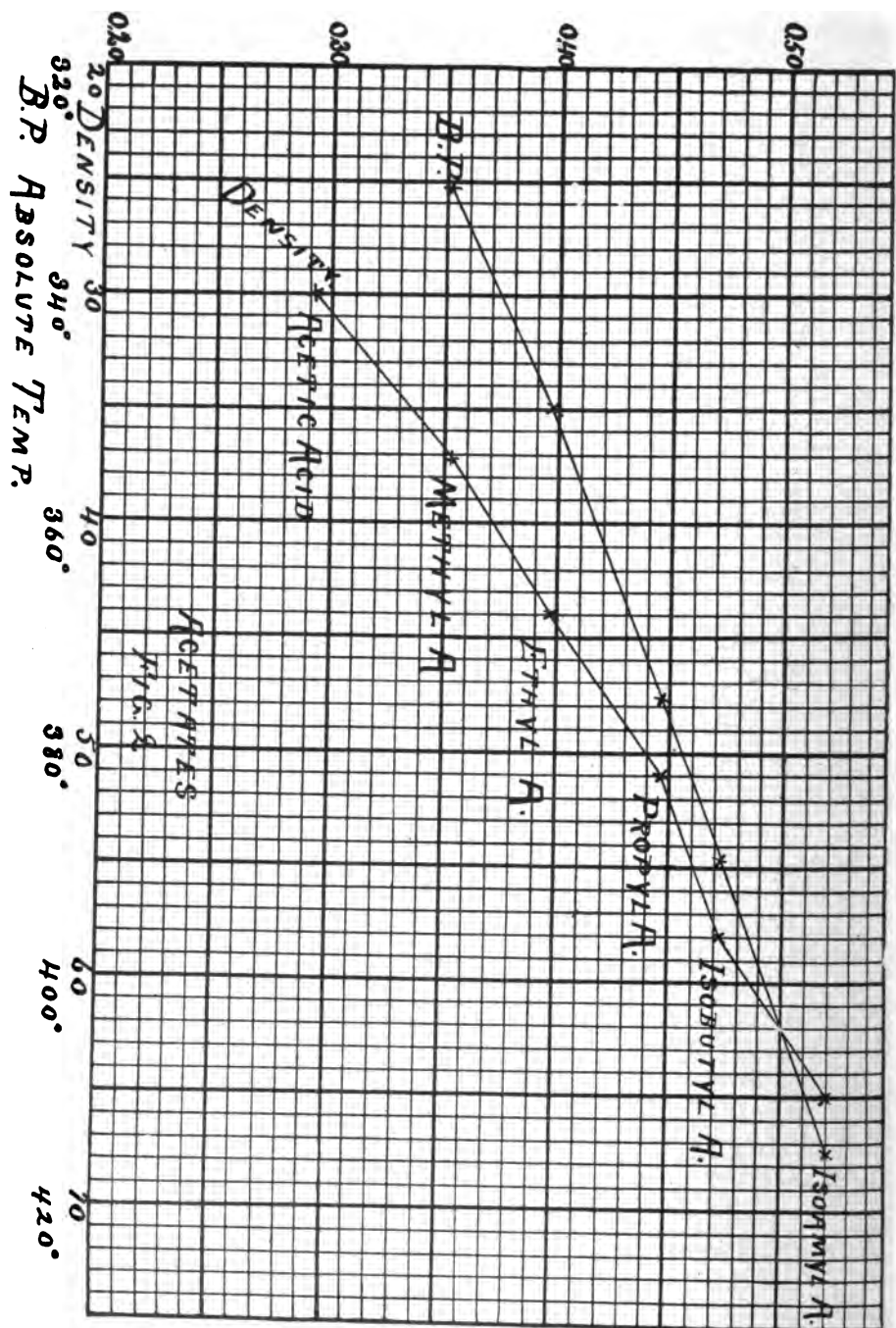


FIG. 2.

since many of Andrews' determinations have been found by later investigators to be considerably too high, it is reasonable to suppose under the circumstances that this one is too high also. To substantiate this I will give the following instances, which may be cited from determinations made by Andrews and Schiff:

Methyl acetate	{	Andrews,	110.20
		Schiff,	93.90-94.0
Ethyl acetate	{	Andrews,	92.68
		Schiff,	83.0-83.1-83.1
Ethyl formate	{	Andrews,	105.30
		Schiff,	92.2-92.1

## ACETATES.

Name.	Formula.	D.	B. P.	S. G.	H. V.	V.	L.
Acetic acid	$\text{HC}_2\text{H}_3\text{O}_2$	30	391.1°	0.9372	101.91 <sup>1</sup>	348.66	0.2923
Methyl acetate	$\text{CH}_3\text{C}_2\text{H}_3\text{O}_2$	37	330.3°	0.8808	93.95 <sup>2</sup>	265.68	0.3536
Ethyl acetate	$\text{C}_2\text{H}_5\text{C}_2\text{H}_3\text{O}_2$	44	350.0°	0.82673	83.1 <sup>2</sup>	209.70	0.3961
Propyl acetate	$\text{C}_3\text{H}_7\text{C}_2\text{H}_3\text{O}_2$	51	375.3°	0.7917	77.3 <sup>2</sup>	173.25	0.4462
Isobutyl acetate	$\text{C}_4\text{H}_9\text{C}_2\text{H}_3\text{O}_2$	58	389.8°	0.7708	69.9 <sup>2</sup>	148.32	0.4713
Isoamyl acetate	$\text{C}_5\text{H}_{11}\text{C}_2\text{H}_3\text{O}_2$	65	415.0°	0.74295	66.35 <sup>2</sup>	127.56	0.5201

The acetates form very good curves, as will be seen in Fig. 2. The boiling-point curve is almost a straight line. It has been shown above that Schiff's determinations of the heats of vaporization (H. V.) of methyl and ethyl acetates are much lower than those of Andrews. Favre and Silberman's determination gives a number for ethyl acetate much higher than that of either of the other investigators, it being 105.8. The results of Schiff are taken as being more nearly correct.

## PROPIONATES.

Name.	Formula.	D.	B. P.	S. G.	H. V.	V.	L.
Propionic acid	$\text{H.C}_3\text{H}_5\text{O}_2$	37	413.7°	0.8589	90.42 <sup>3</sup>	259.08	0.3490
Methyl propionate	$\text{CH}_3\text{C}_3\text{H}_5\text{O}_2$	44	353.0°	0.836798	84.15 <sup>4</sup>	212.25	0.3965
Ethyl	$\text{C}_2\text{H}_5\text{C}_3\text{H}_5\text{O}_2$	51	371.7°	0.7962	77.1 <sup>4</sup>	174.64	0.4415
Propyl	$\text{C}_3\text{H}_7\text{C}_3\text{H}_5\text{O}_2$	58	395.6°	0.76815	71.5 <sup>4</sup>	147.81	0.4832
Isobutyl	$\text{C}_4\text{H}_9\text{C}_3\text{H}_5\text{O}_2$	65	409.8°	0.74424	66.0 <sup>4</sup>	127.78	0.5165
Isoamyl	$\text{C}_5\text{H}_{11}\text{C}_3\text{H}_5\text{O}_2$	72	433.5°	0.7295	63.05 <sup>4</sup>	113.08	0.5576

The curves representing the propionates are shown in Fig. 3, and it will be seen that they are quite regular. The heat of vaporization (H. V.) of propionic acid has never been deter-

<sup>1</sup> Favre and Silberman: *Ann. chim. phys.* [3], 37, 464-470.

<sup>2</sup> Schiff: *Ann. Chem.* (Liebig), 234, 338.

<sup>3</sup> Calculated by the data furnished by the curves shown in this paper.

<sup>4</sup> Schiff: *Ann. Chem.* (Liebig), 234, 338.

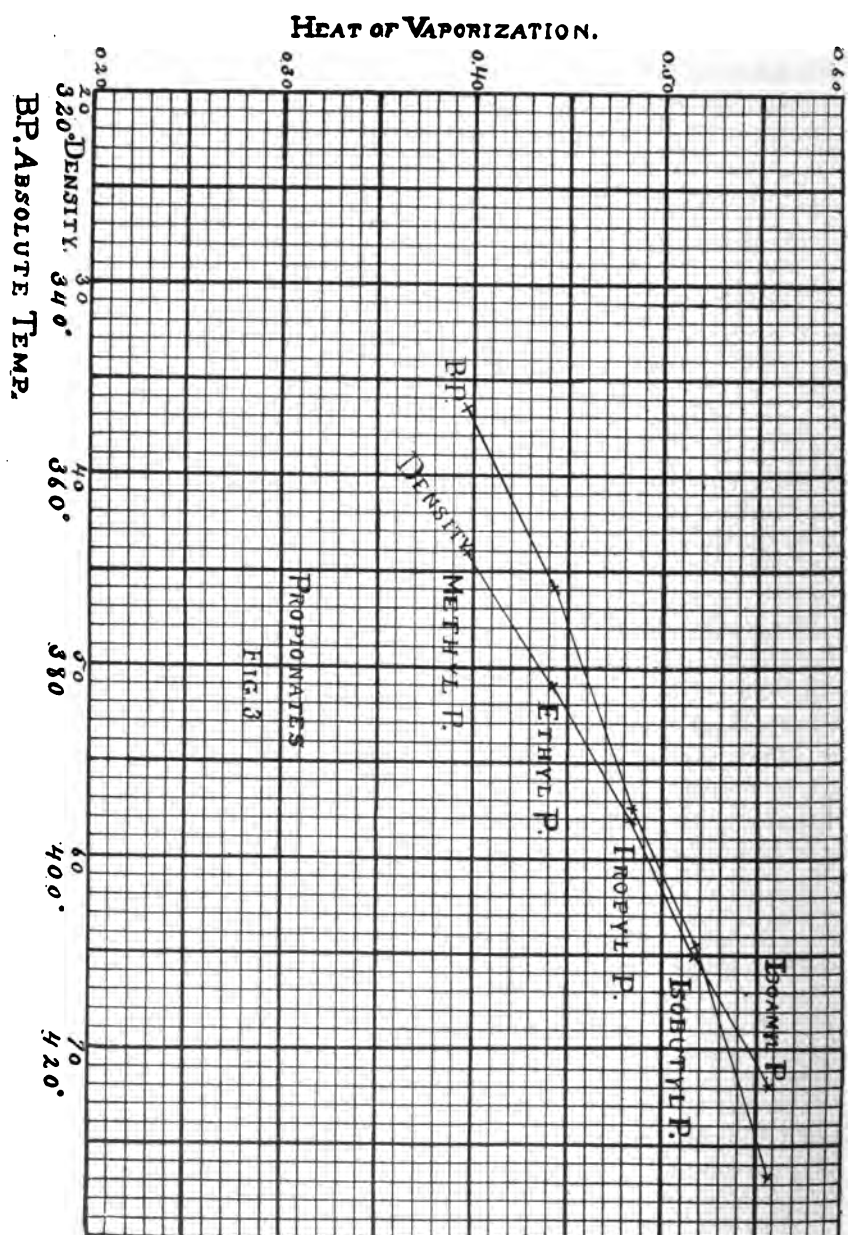


FIG. 3.

mined ; but according to the density curve of the propionates, its heat per unit of volume of vapor (L.) should be 0.3490, which would give for the heat of vaporization (H. V.) the number 90.42.

Name.	Formula.	BUTYRATES.					
		D.	B. P.	S. G.	H. V.	V.	L.
Butyric acid	$\text{H.C}_4\text{H}_7\text{O}_2$	44	435.5°	0.8120	114.67 <sup>1</sup> 82.79 <sup>2</sup>	205.96	0.5567 0.4020
Methyl butyrates	$\text{CH}_3\text{C}_4\text{H}_7\text{O}_2$	51	375.3°	0.80261	87.93 <sup>1</sup> 77.25 <sup>2</sup>	175.64	0.4972 0.4398
Ethyl "	$\text{C}_2\text{H}_5\text{C}_4\text{H}_7\text{O}_2$	58	392.0°	0.7694	71.5 <sup>3</sup>	148.05	0.4829
Propyl "	$\text{C}_3\text{H}_7\text{C}_4\text{H}_7\text{O}_2$	65	416.4°	0.745694	66.2 <sup>3</sup>	128.03	0.5170
Isobutyl "	$\text{C}_4\text{H}_9\text{C}_4\text{H}_7\text{O}_2$	72	429.7°	0.7163	61.9 <sup>3</sup>	111.03	0.5575
Isoamyl "	$\text{C}_5\text{H}_{11}\text{C}_4\text{H}_7\text{O}_2$	79	451.0°	0.71148	59.4 <sup>3</sup>	100.51	0.5910

The curves of the butyrates are shown in Fig. 4. The density curve is almost a straight line, while the boiling-point curve breaks badly at propyl butyrate. This would indicate that its boiling-point, as determined, is too high and should be 408° (absolute temperature) instead of 416.4°, as determined by Linneman, which is given the preference by Carnelley over other determinations. The recorded results of the determinations of the boiling-point of propyl butyrate are as follows :

144.3° C.	Pawlewski.
143.42° C.	Linneman.
142.7° C.	Elsässer.
139°-141° C.	Chancel.
137.25° (765)	Pierre and Puchot.

The last result would agree very well with that deduced from the curve, *viz.*, 135° C.

The heat of vaporization (H. V.) of butyric acid has only been determined by Favre and Silberman. Their result is 114.67 cal., which is probably too high. It gives the heat per unit of volume (L.) 0.5567, which throws it entirely out of the curve shown in Fig. 4, according to which the number should be about 0.4020; this would give 82.79 cal. as the heat of vaporization (H. V.) of butyric acid. As will be seen in the table above Favre and Silberman's result for methyl butyrate is much higher than Schiff's.

<sup>1</sup> Favre and Silberman : *Ann. chim. phys.* [3], 37, 464-470.

<sup>2</sup> Calculated by the data furnished by the curves shown in this paper.

<sup>3</sup> Schiff : *Ann. Chem.* (Liebig), 234, 338.

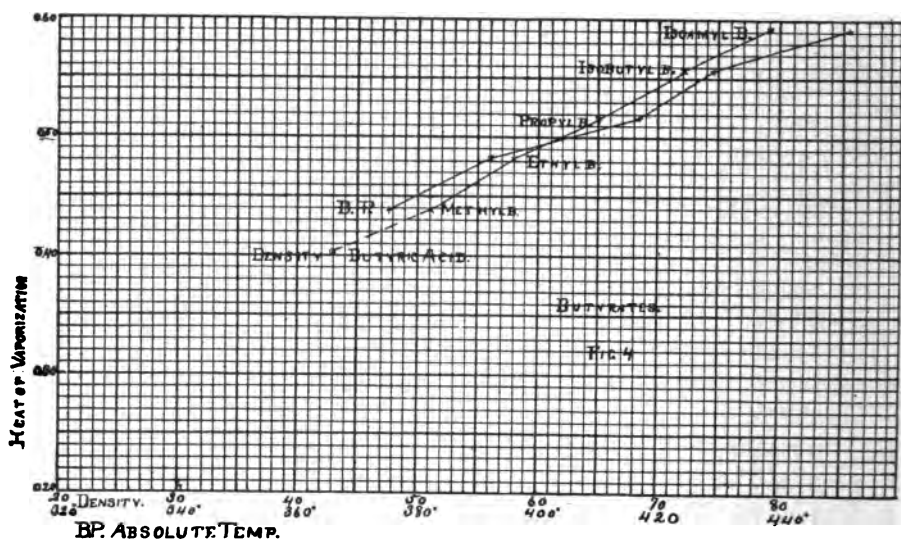


FIG. 4.

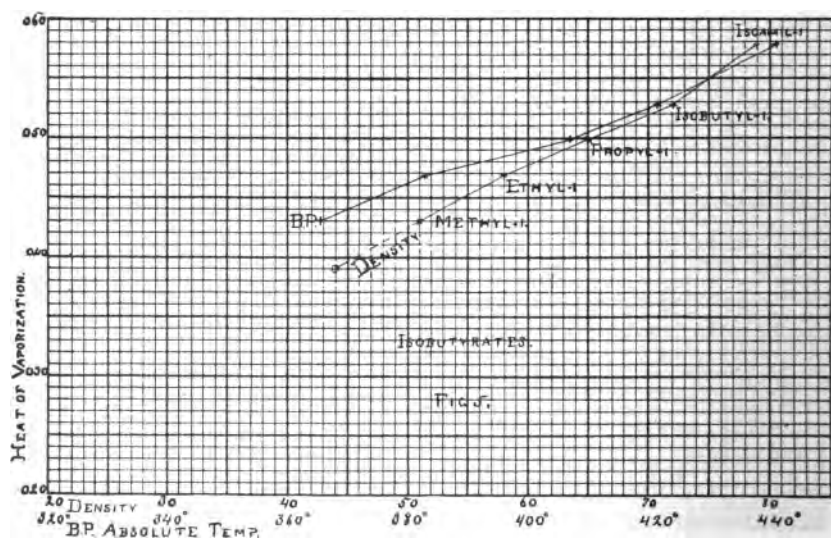


FIG. 5.

## ISOBUTYRATES.

Name.	Formula.	D.	B. P.	S. G.	H. V.	V.	L.
Isobutyric acid	$\text{H.C}_4\text{H}_7\text{O}_2$	44	428.5°	0.8054	76.67 <sup>1</sup>	204.29	0.3900
Methyl isobutyrate	$\text{CH}_3.\text{C}_4\text{H}_7\text{O}_2$	51	365.5°	0.80397	75.5 <sup>2</sup>	175.93	0.4291
Ethyl "	$\text{C}_2\text{H}_5.\text{C}_4\text{H}_7\text{O}_2$	58	383.0°	0.7681	69.2 <sup>2</sup>	147.80	0.4682
Propyl "	$\text{C}_3\text{H}_7.\text{C}_4\text{H}_7\text{O}_2$	65	407.0°	0.74647	63.9 <sup>2</sup>	128.17	0.4985
Isobutyl "	$\text{C}_4\text{H}_9.\text{C}_4\text{H}_7\text{O}_2$	72	421.6°	0.73281	59.95 <sup>2</sup>	113.59	0.5278
Isoamyl "	$\text{C}_5\text{H}_{11}.\text{C}_4\text{H}_7\text{O}_2$	79	441.0°	0.70662	57.65 <sup>2</sup>	99.82	0.5775

The isobutyrate curves (Fig. 5) seem to indicate that the heats of vaporization (H. V.) of the propyl and isobutyl isobutyric rates as determined are a trifle too low. From the density curve it will be seen that the heat per unit of volume (L.) of isobutyric acid should be 0.3900 which would give 76.67 cal. for the heat of vaporization (H. V.). No determination of this constant has been recorded.

## VALERATES.

Name.	Formula.	D.	B. P.	S. G.	H. V.	V.	L.
Valeric acid	$\text{H.C}_5\text{H}_9\text{O}_2$	51	458.4°	0.7828	103.52 <sup>2</sup> 73.83 <sup>4</sup>	171.30	0.6042 0.4310
Methyl valerate	$\text{CH}_3.\text{C}_5\text{H}_9\text{O}_2$	58	389.3°	0.77518	69.95 <sup>2</sup>	149.16	0.4684
Ethyl "	$\text{C}_2\text{H}_5.\text{C}_5\text{H}_9\text{O}_2$	65	407.0°	0.74764	64.65 <sup>2</sup>	128.37	0.5036
Propyl "	$\text{C}_3\text{H}_7.\text{C}_5\text{H}_9\text{O}_2$	72	428.5°	0.727405	61.2 <sup>2</sup>	112.75	0.5427
Isobutyl "	$\text{C}_4\text{H}_9.\text{C}_5\text{H}_9\text{O}_2$	79	442.0°	0.70549	57.85 <sup>2</sup>	99.66	0.5805
Isoamyl "	$\text{C}_5\text{H}_{11}.\text{C}_5\text{H}_9\text{O}_2$	86	460.5°	0.698435	56.2 <sup>2</sup>	90.64	0.6200

The curves representing the valerates are shown in Fig. 6. The density curve is quite uniform. Schiff finds the heat of vaporization (H. V.) of isoamyl valerate to be 56.2 cal. and from the curve it will be seen that the heat per unit of volume (L.) should be 0.6200, but this constant could not be calculated since no determination of the specific gravity of this compound at its boiling-point has been made. However, assuming the curve to be correct, the specific gravity at the boiling-point becomes 0.698435. The only determination of the heat of vaporization (H. V.) of valeric acid on record is that of Favre and Silberman, which places it at 103.52 cal. This would give 0.6042 as the heat per unit of volume (L.), while according to the curve it should be 0.4310, which gives 73.83 cal. as the heat of vaporization (H. V.).

<sup>1</sup> Calculated by the data furnished by the curves shown in this paper.

<sup>2</sup> Schiff: *Ann. Chem.* (Liebig), 234, 238.

<sup>3</sup> Favre and Silberman: *Ann. chim. phys.* [3], 37, 464-470.

<sup>4</sup> Calculated by the data furnished by the curves shown in this paper.

<sup>5</sup> Schiff: *Ann. Chem.* (Liebig), 234, 338.

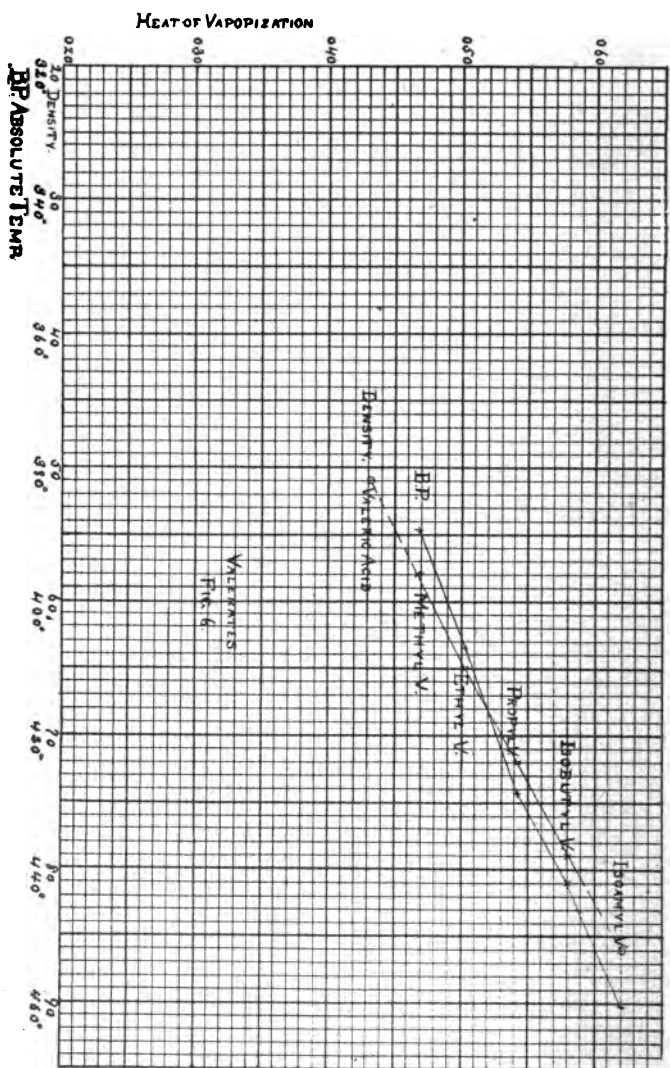


FIG. 6.



According to the boiling-point curve the boiling-point of propyl valerate  $428.5^{\circ}$  (absolute temperature) or  $155.5^{\circ}\text{C.}$  is a trifle too high.

Fig. 7 gives all of the density curves of the compounds above mentioned, in one diagram, showing that the relationship between them is very close and that the uniformity of the curves is very striking.

Fig. 8 is a similar combination of the boiling-point curves, showing the general tread of them to be almost that of a straight line.

## ACIDS.

Name.	Formula.	D.	B. P.	S. G.	H. V.	V.	L.
Formic	$\text{H.CHO}_2$	23	$373.8^{\circ}$	1.1175	$92.71^1$ $120.72^2$	542.26	0.2659 0.2226
Acetic	$\text{H.C}_2\text{H}_3\text{O}_2$	30	$391.1^{\circ}$	0.9372	$101.91^2$	348.66	0.2923
Propionic	$\text{H.C}_3\text{H}_5\text{O}_2$	37	$413.7^{\circ}$	0.8589	$90.42^3$	259.08	0.3490
Isobutyric	$\text{H.C}_4\text{H}_7\text{O}_2$	44	$428.5^{\circ}$	0.8054	$79.67^3$	204.29	0.3900
Butyric	$\text{H.C}_4\text{H}_7\text{O}_2$	44	$435.5^{\circ}$	0.8120	$82.79^3$	205.96	0.4020
Valeric	$\text{H.C}_5\text{H}_9\text{O}_2$	51	$458.4^{\circ}$	0.7828	$73.83^3$	171.30	0.4310

The curves of the acids (Fig. 9) are constructed as far as possible from their constants, as determined and recorded by the various observers, but otherwise the data used have been derived from the curves formed by their corresponding compounds.

The heat of vaporization (H. V.) of acetic acid as determined by Ramsey and Young seems to be too low as it does not conform to either the density or boiling-point curve.

## ALCOHOLS.

Name.	Formula.	D.	B. P.	S. G.	H. V.	V.	L.
Water	$\text{H.OH}$	9	$373.0^{\circ}$	0.9589	$536.0^4$	1189.11	0.4507
Methyl alcohol	$\text{CH}_3\text{OH}$	16	$339.2^{\circ}$	0.7483	$263.86^2$	521.97	0.5055
Ethyl "	$\text{C}_2\text{H}_5\text{OH}$	23	$351.3^{\circ}$	0.74035	$201.42^5$	359.25	0.5607
Isopropyl "	$\text{C}_3\text{H}_7\text{OH}$	30	$355.8^{\circ}$	0.7413	$159.72^5$	275.78	0.5791
Propyl " (nor.)	$\text{C}_3\text{H}_7\text{OH}$	30	$370.1^{\circ}$	0.7366	$164.07^5$	274.03	0.5987
Isobutyl "	$\text{C}_4\text{H}_9\text{OH}$	37	$381.4^{\circ}$	0.7265	$136.16^5$	219.14	0.6213
Butyl " (nor.)	$\text{C}_4\text{H}_9\text{OH}$	37	$389.96^{\circ}$	0.7269	$138.18^5$	219.26	0.6298
Amyl "	$\text{C}_5\text{H}_{11}\text{OH}$	44	$404.4^{\circ}$	0.7154	$118.15^5$	181.46	0.6511

<sup>1</sup> Ramsey and Young: *J. Chem. Soc.*, Lond., 49, 790.

<sup>2</sup> Favre and Silbermann: *Ann. chim. phys.* [3], 37, 464-470.

<sup>3</sup> Calculated by the data furnished by the curves shown in this paper.

<sup>4</sup> Regnault: *Mem. Acad. Sci.*, 21, 638.

<sup>5</sup> Louguine: *Compt. rend.*, 119, 601.

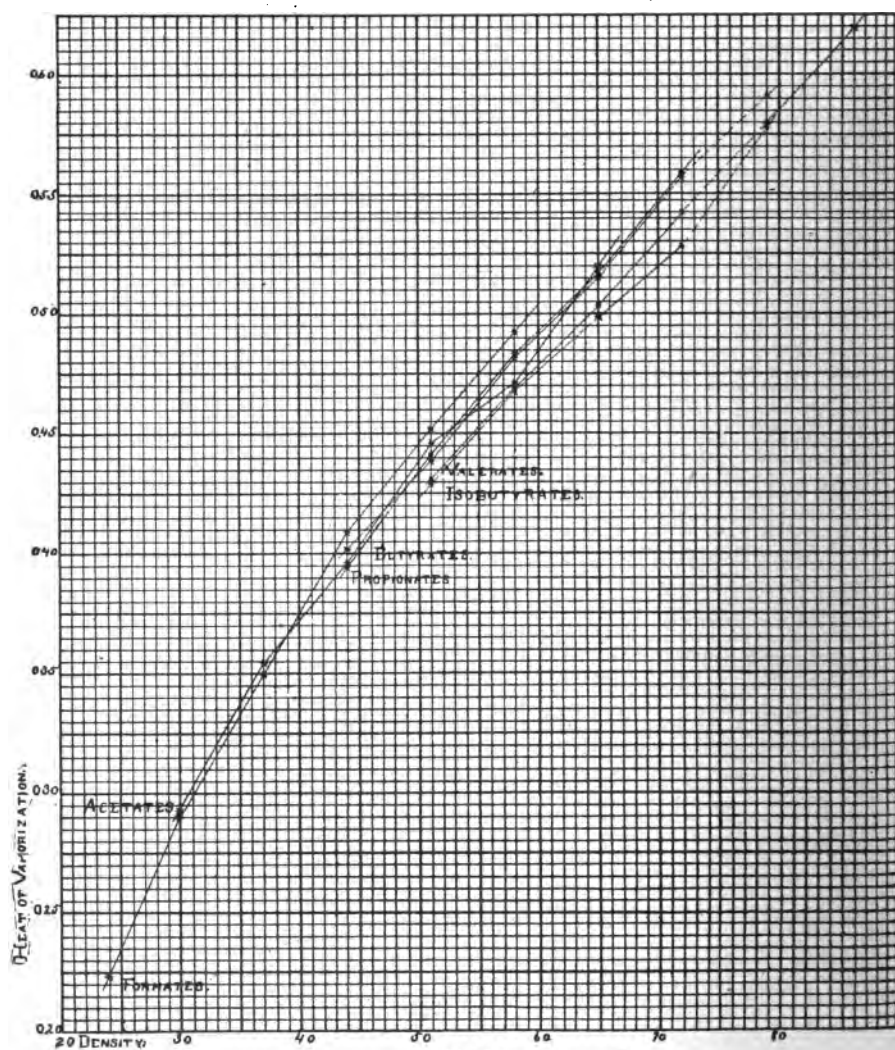
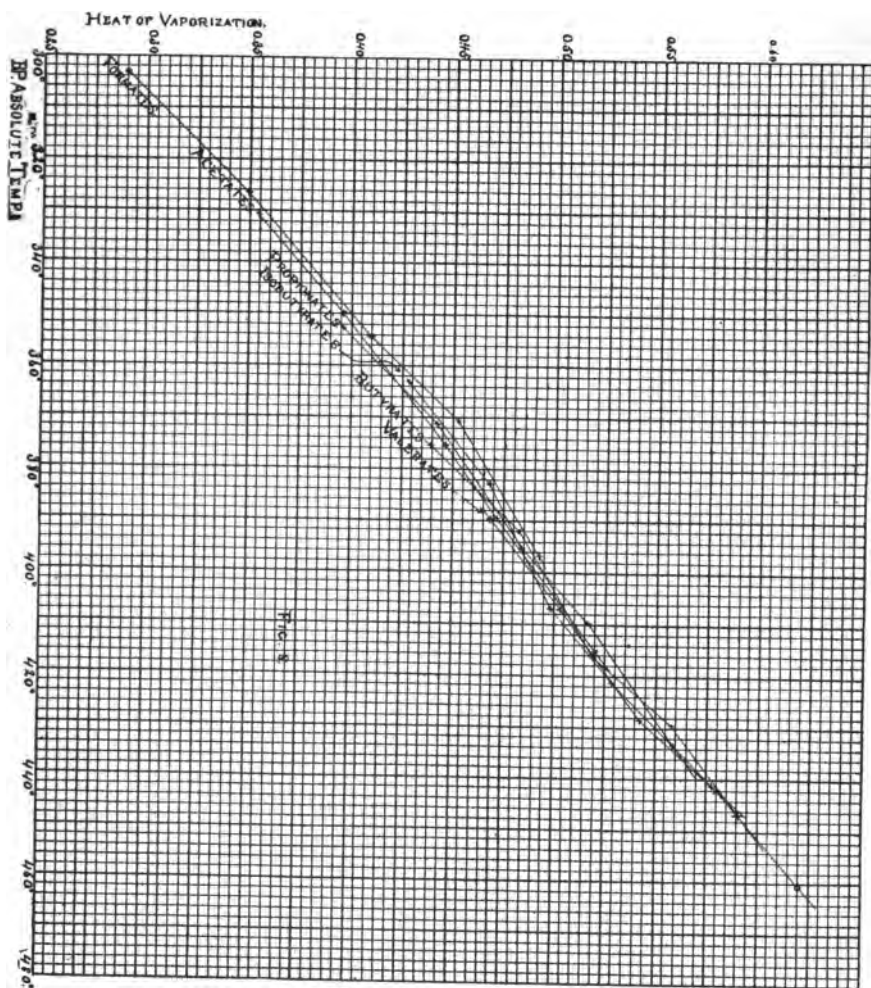


FIG. 7.



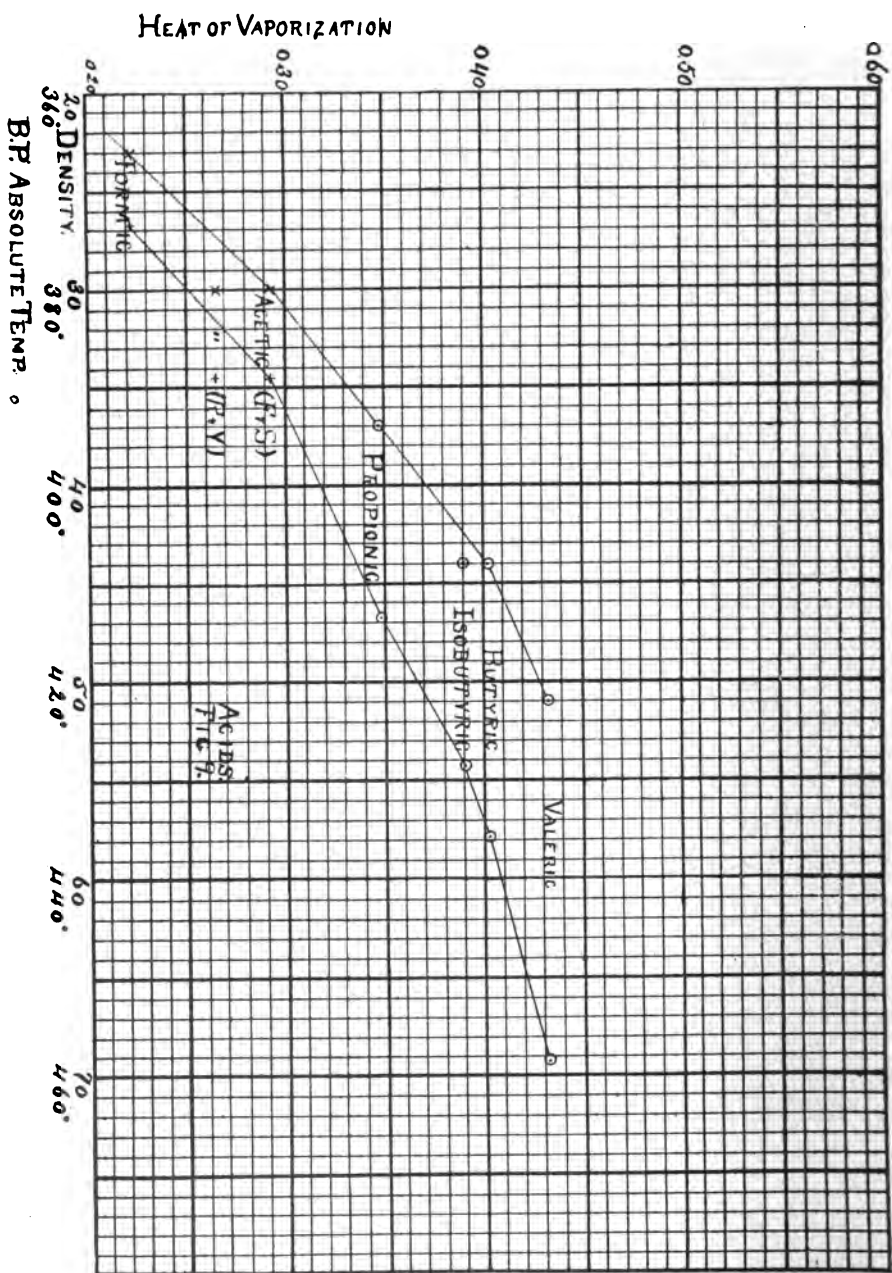


FIG. 9.

The normal alcohols form quite symmetrical curves, as is shown in Fig. 10. In the density curve, water, as the type, falls in with the alcohols as the acids do with their corresponding compounds. It will be noticed that isopropyl and isoamyl alcohols do not fall into line with the normal alcohols, but, as might be expected, they form a portion of a curve for which the data relating to the remaining members of the series are not to be had at present.

In constructing the alcohol curves, the heat of vaporization (H. V.) of methyl alcohol, as determined by Favre and Silberman, was taken in preference to that of Diakonoff, which is believed to be an impossible value. These determinations are as follows :

Favre and Silberman.....	263.86 cal.
Diakonoff .....	123.79 "

In the case of ethyl alcohol the determination of Longuinine was used, although three determinations are recorded as follows :

Favre and Silberman.....	208.92 cal.
Andrews .....	202.40 "
Longuinine .....	201.42 "

Of the two determinations of propyl alcohol (normal)

Diakonoff .....	165.92 cal.
Longuinine .....	164.07 "

I have made use of the latter.

Two determinations of amyl alcohol (by fermentation) are recorded, *viz.*

Favre and Silberman .....	121.37 cal.
Longuinine .....	118.15 "

and I have used the latter.

The determinations of the other alcohols given in the above table have been made only by Longuinine.

#### HYDROCARBONS.

Sufficient data has been found to make it possible to construct curves for a portion of the  $C_nH_{2n-6}$  series of the hydrocarbons, as follows :

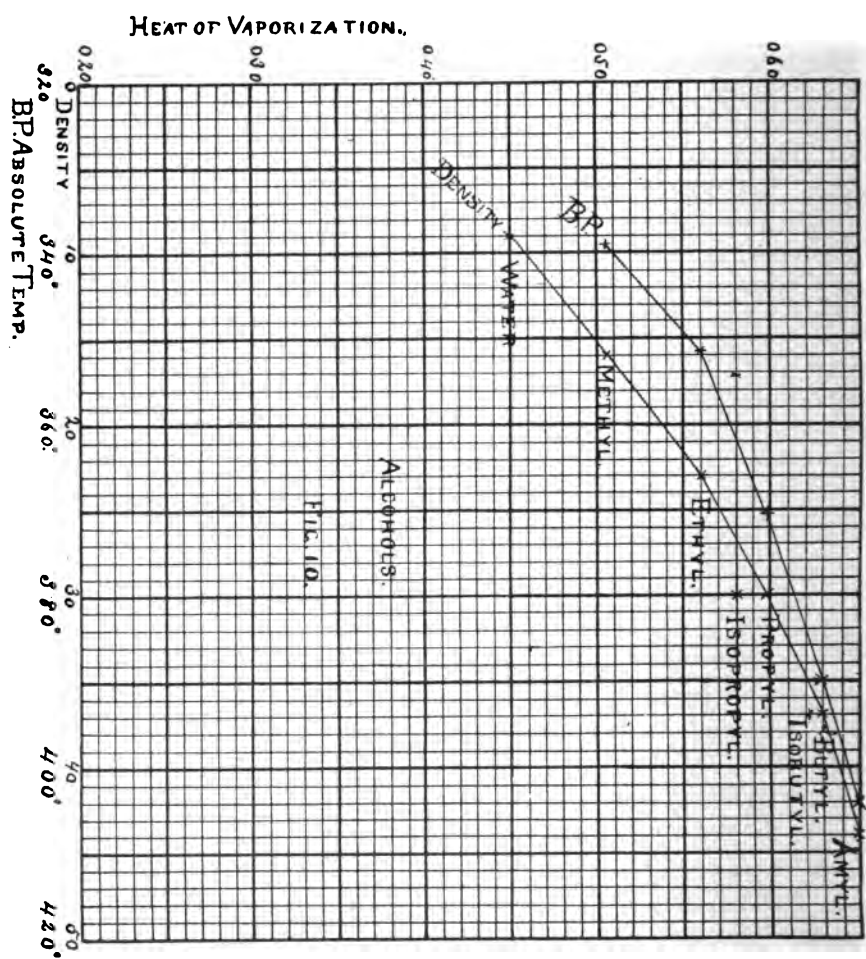


FIG. 10.

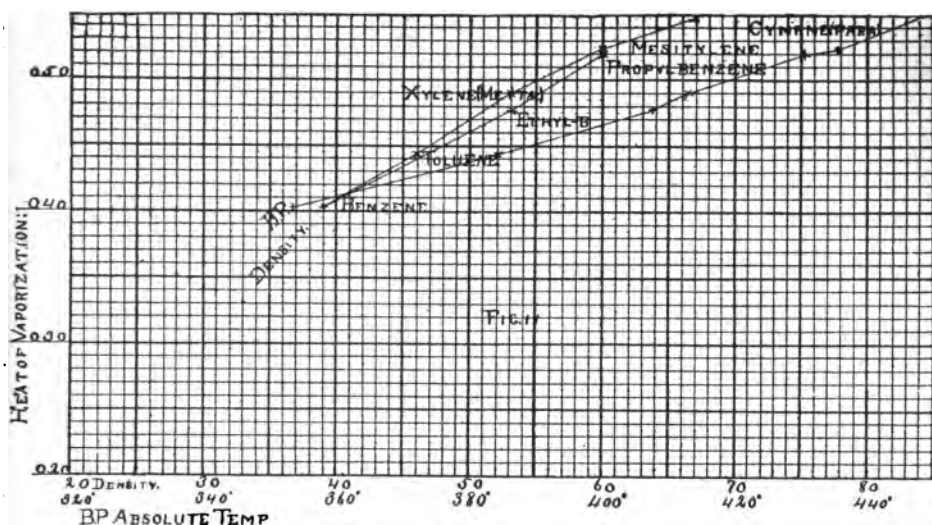


FIG. 11.

Name.	Formula.	D.	B. P.	S. G.	H. V.	V.	L.
Benzene	$C_6H_6$	39	353.35°	0.8111	93.45 <sup>4</sup>	232.11	0.4026
Toluene	$C_7H_8$	46	383.8°	0.77694	83.55 <sup>4</sup>	188.49	0.4432
Ethyl benzene	$C_8H_{10}$	53	407.7°	0.7612	76.4 <sup>4</sup>	160.29	0.4766
Xylene (meta)	$C_8H_{10}$	53	412.9°	0.75715	78.25 <sup>4</sup>	159.44	0.4908
Propyl benzene	$C_9H_{12}$	60	430.2°	0.7399	71.75 <sup>4</sup>	137.63	0.5213
Mesitylene	$C_9H_{12}$	60	435.7°	0.7372	71.75 <sup>4</sup>	137.12	0.5232
Cymene	$C_{10}H_{14}$	67	448.0°	0.7248	66.3 <sup>4</sup>	120.73	0.5491

As will be seen in Fig. 11 these hydrocarbons form two density curves; one is formed by benzene, ethyl benzene, and propyl benzene, and the other by benzene, toluene, xylene, mesitylene, and cymene. The boiling-point curve is fairly regular and contains all of the series.

## CONCLUSION.

From the foregoing we may enunciate the following law, *viz.* :

"In any homologous series, the heat of vaporization in a unit of volume of the vapor, under the same conditions as to temperature and pressure, is proportional to the density and also to the absolute boiling-point."

It will be noticed that the acid radical in any series fixes the

<sup>4</sup> Schiff: *Ann. chem.* (Liebig), 234, 338.

characteristic of the curve, *i. e.*, the acid radical is the basis of the structure of the molecule, and the bases in combination with it, do not alter the general molecular architecture.

When more complete data have been obtained some interesting developments in this direction may be expected.

VANDERBILT UNIVERSITY.

## THE DETERMINATION OF METHANE AND HYDROGEN BY EXPLOSION.<sup>1</sup>

BY AUGUSTUS H. GILL AND SAMUEL P. HUNT.<sup>2</sup>

Received September 26, 1895.

IN making an analysis of illuminating gas by Hempel's method it was noticed that the determination of the constituents by explosion was by no means as accurate as that made by absorption. This had been observed by Hinman<sup>3</sup> and is probably due (1) to the fact that an aliquot part of the residue (after all absorptions had been made) containing the methane and hydrogen is used, necessitating the multiplication of errors by a factor as large as four or five, and (2) to the possible absorption of the carbon dioxide formed by the water in the burette. To obviate these difficulties, it was determined to use all the gas left after the absorptions had been made, mercury as the confining liquid and to explode with pure oxygen rather than with air. Instead of using the gas left after the actual absorptions, which would be of unknown composition and troublesome to obtain, an artificial mixture, made from methane, hydrogen and nitrogen, approximating closely to the composition of the residue, was employed.

*Preparation of the Gaseous Mixtures.*—The hydrogen was prepared by the electrolysis of water; it was then shaken up with potassium pyrogallate to remove the slight quantity of oxygen with which it was mixed, and upon analysis was found to contain four and two tenths per cent. of nitrogen. In making an analysis of hydrogen, we would lay especial emphasis upon the necessity of having the ratio of explosive mixture to inert gases as great as 1:6 as Hempel<sup>4</sup> recommends, in order not to burn the nitrogen.

<sup>1</sup> Prepared for the Springfield Meeting, August 28, 1895.

<sup>2</sup> The work described in this paper formed the basis of a thesis presented by Mr. Hunt to the Faculty of the Massachusetts Institute of Technology for the Degree of Bachelor of Science.

<sup>3</sup> Massachusetts Senate Document No. 16, 1892. *Inspection of Gas and Gas Meters*, p. 12.

<sup>4</sup> Hempel, "*Gasanalytische Methoden*" p. 132.



This is considerably larger than that which Bunsen<sup>1</sup> recommended, which may vary between the limits twenty-six and sixty-four of combustible gas to 100 of incombustible. Unless the larger ratio be adopted the determination of hydrogen may come two and a half per cent. high, as is shown by the following table:

TABLE I. DETERMINATION OF THE PURITY OF THE HYDROGEN.

Hydrogen taken cc.	Air used cc.	Ratio.	Per cent. hydrogen.
20.5	185.0	1 : 5.7	95.8
20.5	185.0	1 : 5.7	95.8
50.0	115.0	1 : 1.2	98.3
50.0	115.0	1 : 1.2	98.0

The nitrogen probably burns to  $N_2O_5$ , as the characteristic dark red fumes of this gas were frequently seen in the pipette. By the Griess test with  $\alpha$ -naphthylamine we were able to prove the presence of quite a quantity of nitrites in several cases.

In making the analyses of hydrogen by the first method it was necessary to connect and disconnect the burette three times in each case; the error which might be introduced was determined with the following results:

TABLE II. SHOWING THE ERRORS IN MANIPULATION IN CONNECTING THE BURETTE AND PIPETTE.

Burettefuls.	Air put in cc.	Air taken out cc.	Errors cc.	Remarks.
3	210.3	207.4	-2.9	No connections wired.
3	216.0	216.6	+0.6	
3	210.2	208.7	-1.5	
3	213.3	213.8	+0.5	All connections wired but one.
1	97.6	97.2	-0.4	
1	97.2	96.8	-0.4	All connections wired.
3	237.5	237.3	-0.2	

The oxygen was obtained in a similar manner to the hydrogen and contained one and six-tenths per cent. hydrogen and one and four-tenths per cent. nitrogen. The nitrogen in both these gases probably came from the distilled water electrolyzed, which was not freshly boiled before use.

The nitrogen employed was prepared by removing the oxygen from the air by means of phosphorus, allowing the gas to stand in the light twenty-four hours to decompose any ozone, and subsequent treatment with a small quantity of alkaline pyrogallate.

<sup>1</sup> Bunsen, "Gasometrische Methoden" (1877) p. 73.

An attempt was made to prepare the methane by the usual method of heating sodium acetate with sodium hydroxide and quicklime; the gas was found to be so largely contaminated with hydrogen,—as high as ten per cent. being found—as to be unfit for our purpose. This result is directly at variance with the statement of Freyer and Meyer<sup>1</sup> who say that this process “furnishes a very approximately pure gas.”

Nor did the method of Gladstone and Tribe,<sup>2</sup> the reaction of a zinc-copper couple upon methyl iodide, at first yield any better results, owing possibly to the water in the alcohol used. To obviate this and also prevent the possible formation of ethane, anhydrous methyl alcohol was substituted for the ordinary alcohol usually employed. The air in the apparatus was displaced by carbon dioxide and the methane collected, treated with potassium hydroxide to absorb this impurity. An analysis of the gas thus made, by explosion with oxygen and also with air—care being taken to avoid burning any nitrogen—showed the methane to be chemically pure.

The gases thus prepared and also the mixtures made from them, were stored in bottles provided with doubly-perforated rubber stoppers carrying a tube for the introduction of water and a tube for the egress of the gas. To render these absolutely tight, the stoppers were fastened in by fitting a brass plate to cover the top of the stopper, and by means of brass bolts and nuts passing through wire loops around the neck of the bottle, pressing the stopper firmly into the neck of the bottle. Joints of this kind are sufficiently tight to withstand a pressure of hydrogen.<sup>3</sup> To reduce the possibility of the transfusion of the gases to a minimum, a slight outward pressure was maintained in each bottle and it was inverted in a pan of water. The separate gases were kept in this way for about two months, freshly distilled water being used to displace the quantities requisite for the various mixtures. These mixtures made from them stood in no case over two days, before being completely used up, so that the amounts of methane and hydrogen dissolved by the distilled water, used to displace the various volumes taken, were negligi-

<sup>1</sup> *Ztschr. phys. Chem.*, 11, 28.

<sup>2</sup> *J. Chem Soc.*, 45, 154.

<sup>3</sup> Gill: *J. Anal. Appl. Chem.*, 6, 601.

ble ; the coefficients of absorption of the various gases not being widely different the ratio of the gases would remain the same within the errors of the analysis.

The gases were mixed by displacing the water from a liter bottle with the proper amounts of methane, hydrogen and nitrogen—measured by a burette—care being taken to leave some of the water to act as a stirrer, and then thoroughly shaking the bottle. By connecting this with a bottle of distilled water by means of a siphon, the requisite quantity of gas for an experiment could be displaced into the burette.

*Method of Procedure.*—Fifty cubic centimeters—this being about the usual residue from Boston gas after all the absorbable constituents had been removed—were measured out, mixed with about sixty cc. of oxygen and burned in an explosion pipette devised by one of us.<sup>1</sup> This combustion took place in different ways, at first as one explosion, and later by two explosions, with the idea of diminishing the error due to the possible combustion of nitrogen. In using the latter method it was found necessary to make the ratio of the explosive mixture to inert gases, nearly 1 : 2 in order that any explosion might take place ; with some mixtures not strong enough to explode, if care be not taken to pass the spark but a short time, the fine platinum wire becomes heated and finally glows, similar to the platinum sponge in the Döbereiner lamp, producing a very slow combustion, causing annoyance and delay in the analysis. A rough experiment may very well be made at first, to determine the composition of the gas under investigation and then suitable quantities of oxygen added for the first and second explosion.

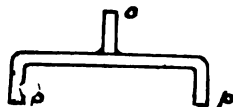
The residue in the explosion pipette was, in every case, transferred to an ordinary Hempel burette for measurement, mercury, instead of water, being the confining liquid ; the gas was passed into potassium hydroxide and then into pyrogallate for the determination of carbon dioxide and oxygen. It is almost impossible to avoid sucking back some of the absorbents into the burette, which being strongly alkaline, would vitiate the next analysis by absorbing carbon dioxide ; to obviate this difficulty the instrument was washed out with dilute acetic acid<sup>2</sup> and then with

<sup>1</sup> Gill : *J. Am. Chem. Soc.*, 17, 771.

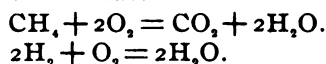
<sup>2</sup> If hydrochloric acid be used it forms a precipitate of mercurous chloride upon the walls of the pipette, coming from the mercurous salts produced by the action of the oxides of nitrogen upon the mercury.

water, almost filled with mercury allowed to stand about half an hour, the water which collected at the top displaced and then used for the next determination.

Instead of using the ordinary doubly bent connecting tube, this was varied by the introduction of a T joint, which is found especially convenient in adding successive portions of oxygen. The burette being connected at b, the pipette at p, and the oxygen at o, one can add the oxygen without disconnecting the burette each time. By connecting in a short tube at o, and filling it with mercury, the capillaries can be filled with mercury, an important point in preventing the rubber connectors from being burst by the force of the explosion. All connections should be carefully wired. By the use of two sets of apparatus two analyses may be executed at one time, in one an absorption be taking place, in another an explosion, etc. Six analyses in three hours were frequently made.



*Calculation of Results.*—The calculation of the results of the explosion was made according to the directions of Hempel,<sup>1</sup> that is in accordance with the reactions :



The volume of carbon dioxide obtained represents the methane present, and twice this volume subtracted from the total contraction, gives the contraction due to hydrogen; this latter being multiplied by two-thirds, gives the amount of hydrogen present. Table III shows the results obtained.

TABLE III.—ANALYSIS OF A MIXTURE OF METHANE, HYDROGEN AND NITROGEN BY ONE EXPLOSION WITH OXYGEN.

Mixture cc.	Oxygen per cent.	Methane per cent.	Hydrogen per cent.	Nitrogen per cent.
49.8	65.2	34.7	54.8	10.5
51.9	65.0	35.3	54.1	10.6
49.7	65.6	35.1	53.9	11.0
50.1	61.3	34.5	55.0	10.5
51.5	61.8	35.0	53.6	11.4
59.4	72.8	34.4	55.0	10.6
49.4	56.2	34.3	55.0	10.7
49.2	56.0	34.0	54.9	11.1
49.2	58.3	33.4	55.0	11.6
49.9	55.6	34.8	54.9	10.3
	Average	34.5	54.7	10.8
	Theory	34.7	53.5	11.8

<sup>1</sup> *Loc. cit.*, 217.

The results obtained in the estimation of the methane are quite satisfactory and are probably within the limits of error of the apparatus. The hydrogen is high, due to the fact that the methane is low, and possibly also to the burning of the nitrogen.

In order to diminish the error from the latter source, a new mixture was made, and analyzed by exploding twice successively with oxygen, care being taken to add as little oxygen for the first explosion as would make the mixture combustible. Table IV shows the results obtained.

TABLE IV.—ANALYSIS OF A MIXTURE OF METHANE, HYDROGEN AND NITROGEN BY TWO EXPLOSIONS WITH OXYGEN.

Mixture cc.	Oxygen used		Methane per cent.	Hydrogen per cent.	Nitrogen per cent.
	first time.	second time.			
51.2	40.0	40.9	32.6	46.6	20.8
51.1	41.0	39.9	32.0	46.5	21.5
56.7	40.0	50.3	32.1	46.7	21.2
48.5	31.0	45.7	32.2	47.5	20.3
50.3	31.0	49.8	32.4	48.0	19.6
50.9	32.0	51.1	32.3	47.6	20.1
53.4	35.0	45.6	31.7	48.1	20.2
50.9	30.0	52.9	32.1	48.1	19.8
49.3	29.0	47.7	32.2	47.9	19.9
50.7	31.0	49.6	32.3	48.5	19.2
Average			32.2	47.55	20.25
Theory			32.2	47.7	20.1

The results are very satisfactory and if we compare them with those of the preceding table (III), we see that the average is more nearly correct than that of the former, and the deviations from the mean much less. The first three present the greatest variation in regard to hydrogen, it being one per cent. too low, these two had the greatest proportional amount of oxygen in the first explosion which is anomalous.

In order to obtain an idea of what takes place during the first explosion, several were performed and the per cents. of methane and hydrogen which burned determined.

TABLE V.—SHOWING THE AMOUNT OF METHANE AND HYDROGEN BURNED WHEN AN INSUFFICIENT QUANTITY OF OXYGEN IS PRESENT.

mixture cc.	oxygen cc.	Methane			Hydrogen		
		present cc.	burned cc.	burned per cent.	present cc.	burned cc.	burned per cent.
53.0	29.2	17.1	4.0	23.4	25.0	12.5	50.0
53.4	29.1	17.2	4.3	25.0	25.2	11.7	46.3
55.0	33.6	17.7	4.9	27.7	26.0	16.7	64.3
57.4	35.2	18.5	5.2	28.1	27.1	17.0	63.8

About sixty per cent. of the hydrogen burned and, contrary to the usual opinion, twenty-five per cent. of the methane and only about fifty per cent. of the oxygen.

By way of comparison with the usual method, a series of analyses of the same mixture was carried through, employing a smaller quantity and exploding with air; the mercury explosion pipette was used as before and the residue after explosion measured in a burette using water, as is customary, instead of mercury as the confining liquid.

TABLE VI.—ANALYSIS OF A MIXTURE OF METHANE, HYDROGEN AND NITROGEN BY EXPLODING WITH AIR.

Mixture cc.	Air cc.	Methane per cent.	Hydrogen per cent.	Nitrogen per cent.
17.8	79.8	29.8	45.3	24.9
15.3	82.2	31.4	49.3	19.3
16.3	81.4	33.7	42.5	23.9
15.9	82.4	31.4	38.6	30.0
16.1	78.2	39.1	30.4	30.5
16.8	80.5	33.3	42.3	24.4
16.1	82.0	30.4	44.1	25.5
16.2	81.2	36.4	33.4	30.2
15.8 <sup>1</sup>	79.5	31.6	40.0	28.4
15.1	82.5	33.8	38.0	28.2
16.2	82.6	31.2	42.9	25.9
14.8	83.8	34.4	38.4	27.2
15.9	84.3	33.9	37.7	28.6
	Average	33.1	42.2	26.7
	Theory	32.2	47.7	20.1
	Deviation	+0.9	-7.5	+6.6

These figures substantiate those of Hinman,<sup>2</sup> the results for methane and nitrogen being high and those for hydrogen low, the variations between the different analyses are even more marked. It is to be noticed that, contrary to expectation, the results upon the methane are high, indicating perhaps that the water in the burette is without appreciable solvent action upon the carbon dioxide formed. The discrepancy in the estimation of hydrogen is explained by the increase in the percentage of methane, any increment here being first doubled and subtracted from the "total contraction," and then approximately doubled in making the calculation, lowering as a consequence the hydro-

<sup>1</sup> These last five were measured after explosion with the mercury burette.

<sup>2</sup> *Loc. cit.*

gen by about four per cent., leaving three and five-tenths per cent. to be accounted for.

Almost the only supposition to account for this phenomenon is the somewhat anomalous one, that under these conditions the hydrogen is not completely burned.

In order to determine the effect of certain errors, such as the reading of the burette—graduated in fifths of a cubic centimeter—and any mistakes made in transferring the gases, the following assumptions were made (Table VII), and the deviations these might produce were calculated by the method of least squares, with the results showed in Table VIII.

TABLE VII.—SHOWING THE VOLUME OF GASES TAKEN AND THE ERRORS ASSUMED IN THEIR MEASUREMENT AND MANIPULATION.

	Oxygen method. cc.	error.	Air method. cc.	error.
Gaseous mixture taken.....	50.	0.15	15.	0.15
Oxygen (or air) used .....	60.	0.15	85.	0.15
Residue after explosion.....	33.	0.25	21.	0.25
Carbon dioxide formed.....	16.	0.25	5.	0.25

TABLE VIII.—SHOWING THE DEVIATIONS TO BE EXPECTED IN THE DETERMINATIONS OF THE VARIOUS GASES UPON THE ASSUMPTIONS IN TABLE VII.

	Oxygen method. per cent.	Air method. per cent.
Methane.....	0.51	1.64
Hydrogen .....	0.82	2.40
Nitrogen (by difference) .....	1.70	4.30

The results of this investigation may be summarized as follows:

- (1) The method of preparation of methane by heating sodium acetate, hydroxide and lime together does not yield a pure gas.
- (2) The method of determination of methane and hydrogen by one explosion yields results accurate to less than five-tenths per cent. of the methane and three-tenths per cent. of the hydrogen.
- (3) The method by two explosions yields results with in two-tenths per cent. of methane and three-tenths per cent. of the hydrogen.
- (4) When a mixture of hydrogen and methane is exploded with a quantity of oxygen insufficient for both, but more than sufficient for either, about sixty per cent. of the hydrogen and

twenty-five per cent. of the methane and fifty per cent. of the oxygen are consumed.

(5) The method of determination of the gases by one explosion with air gives results not within nine-tenths per cent. of the methane and seven and five-tenths per cent. of the hydrogen.

In concluding this article we would express our indebtedness to Mr. R. B. Price for preliminary work which served as the foundation of this thesis.

---

### NEW BOOKS.

A MANUAL OF QUALITATIVE CHEMICAL ANALYSIS. BY E. P. HARRIS, PH.D., LL.D., Professor of Chemistry in Amherst College. New edition. Thoroughly revised and corrected. Amherst, Mass.: Carpenter & Morehouse. 1895. pp. 308. Price \$1.50.

The author of this book is a veteran teacher, and this new edition is the result of the experience of his laboratory teaching for over a third of a century. The book is divided as follows:

Part I. Examination of solutions: Sec. I, Bases; Sec. II, Acids.

Part II. Examinations of solids.

Part III. Qualitative separations: Sec. I, Bases; Sec. II, Acids.

Supplement: Reaction of rare elements; Use of the spectro-scope in analysis.

Appendix: Preparation of reagents; Table of solubility; Index.

Part first gives the reactions of each of the metals and acids, and is interleaved that the student may write out the reaction-equations on the blank pages. This is intended to be used in connection with unknown solutions containing a single base and acid.

Part second is a guide to the systematic examination of solids according to the plan which was first introduced by the author and has since been very generally adopted. This is perhaps the most valuable part of the book.

Part third takes up the separations of metals systematically, using the methods which have proved most satisfactory in the Amherst laboratory. Alternate methods are in a number of instances given, but generally only a single method; the idea is to avoid confusing the student with a number of different ways of working, the relative merits of which he is incapable of estimating. This part is very complete, covering practically all cases



with the common metals and acids, while it is well supplemented by a very comprehensive chapter on the reactions of the rare metals.

The appendix on the preparation of reagents will be found useful to teachers.

This manual is not intended to merely make the student a good analyst ; it is rather a manual of instruction in chemistry through the medium of qualitative analysis. It is not a book for self-instruction, but it is intended that the student shall have the constant supervision of an instructor. As a manual for college students it does not appear to be too much to say that of all the many books of its class it is the best.

JAS. LEWIS HOWE.

PRINCIPLES AND PRACTICE OF AGRICULTURAL ANALYSIS. BY HARVEY W. WILEY. VOL. II. FERTILIZERS. Cloth, 8 vo. pp. 332. Easton : Chemical Publishing Co. 1895. Price, \$2.00.

The official inspection of fertilizers involves such great pecuniary interests that the chemical methods used for the purpose are matters of the highest importance to analyst and manufacturer. All countries in which fertilizers are used to any extent have some plan of inspection and certain methods of conducting the chemical work required. These methods are the result of very numerous and often difficult investigations of the men best qualified to deal with the subject.

In the volume under consideration the subject of fertilizers is treated under four heads : (1) Phosphates and phosphatic fertilizers ; (2) Nitrogen in fertilizers and fertilizing materials ; (3) Potash in fertilizing material and fertilizers ; (4) Miscellaneous fertilizers, lime, gypsum, ashes, coarse manures, etc.

The matter of drawing samples of various materials receives a deservedly large share of attention. Then the analytical work proper is taken up and treated very fully and clearly. The different analytical methods of various countries are given in full and a brief but very valuable discussion of the merits of the methods follows. In many cases the value of the discussion is increased by full statements of analyses.

The matter thus brought together consists of both original matter and material published at home and abroad ; and often published in such a way as to be now inaccessible to many workers on the subject.

The treatment of the subject is full, clear, systematic, and well up to date. Enough technology is included to show the reader the reason for the methods used in the work ; and the author has not lost sight of the fact that he is writing on the principles as well as the practice of agricultural analysis.

The chemist who has been unfortunate enough to buy a number of alleged treatises on agricultural chemical analysis (chiefly of English origin) that have recently appeared will fully appreciate the merits of this work and heartily thank Dr. Wiley for producing a work that is full and reliable. For if the investigator of questions bearing on the analysis of fertilizing material does not find here methods suitable for the purpose he has in view, he may as well resign himself to working the matter out for himself.

To the teacher the book is of very great value, and if used by students they will have the satisfaction of knowing that they are well prepared for technical work in factory or inspection laboratories.

The full citation of authorities and an unusually complete table of contents and index are commendable features of the work.

In the preface, the author regrets "that the contents of the volume have again exceeded all expectations." His readers will not share this regret, for there is nothing here that could have been omitted to advantage.

It is to be hoped that there may be no delay in the appearance of the remaining volumes of a work that is of such high value to those who wish to keep informed on so wide a range of chemical work as is included under the term agricultural analysis.

H. A. HUSTON.

LABORATORY WORK IN CHEMISTRY. A SERIES OF EXPERIMENTS IN GENERAL INORGANIC CHEMISTRY. BY EDWARD H. KEISER. 8 vo. viii, 119 pp. New York: American Book Co.

This little book, in spite of its name, is not exclusively a laboratory guide nor is it exclusively devoted to experiments in inorganic chemistry. Thus, we find (p. 62) a definition of *equivalent*, and a description of the properties of carbon (p. 94). The experiments relating to the organic compounds, marsh gas,

ethylene, and calcium carbide do not strike one as being very instructive or *apropos* of anything in particular.

An excellent feature is the introduction of numerous questions, although these might, perhaps with advantage, have been more closely confined to the subjects of the experiments. It is not easy to see, for example, why such a question as the following should be brought into a laboratory manual: "Which elements make up three-fourths of the solid crust of the earth?"

A number of the more difficult experiments, such as the gravimetric determination of the composition of water are to be performed by a few more advanced students for the benefit of all, a commendable arrangement when the classes are not too large.

The experiments are, in the main, well selected and described in simple and clear English. The use of the term "arseniu-retted hydrogen" is a curious anachronism in a book which for the rest adheres to a modern nomenclature.

L. W. ANDREWS.

---

#### BOOKS RECEIVED.

Kentucky Agricultural Experiment Station, Bulletin No. 56. Analysis of Commercial Fertilizers. Lexington, Ky.

Kentucky Agricultural Experiment Station, Bulletin No. 57. (1) Wheat Experiments. (2) Oat Experiments. Lexington, Ky.

Texas Agricultural Experiment Station, Bulletin No. 36. Vegetable Insecticides. College Station, Brazos County, Texas.

---

#### NOTE.

*The Banquet to Messrs. Mond and Tyrer.*—Two prominent English chemical manufacturers, Messrs. Ludwig Mond, a member of the well-known firm of Brunner, Mond & Co., and Thomas Tyrer, a manufacturer of pharmaceutical chemicals and now President of the Society of Chemical Industry, have been paying a visit to the United States. There has naturally been considerable desire among American chemists to meet these gentlemen, and they have received many invitations and courtesies. An account of Mr. Tyrer's visit to the meeting of the

Lehigh Valley Section of the American Chemical Society will be found in the Proceedings issued with the November number of this Journal.

On the evening of November 1, ninety-one chemists took part in a farewell banquet at Delmonicos. The after-dinner speakers were Mr. Alfred Mason, of New York, who presided, Thomas Tyrer, Ludwig Mond, Peter Townsend Austen, Seth Low, W. H. Nichols, and H. W. Wiley. Impromptu remarks were also made by J. H. Appleton and Walter H. Bunn. A verbatim account of the remarks made is contained in the *New York Oil, Paint and Drug Reporter*, November 4, from which this account is condensed.

It is quite impossible in the space available to do justice to all that was said. The addresses made were all enjoyable, some of them brilliant, and the festivities were ably and wittily directed by Mr. Mason.

Mr. Tyrer, who spoke for the Society of Chemical Industry, after referring to the early history of the Society, expressed his appreciation of the courtesies received during his visit, his belief in the greatness of our industrial future, and his admiration of our institutions of learning.

Professor Austin spoke for the N. Y. Section of the American Chemical Society. Among other things, he said:

"In this country the practical chemist and the teacher have little time left for purely scientific research and in this we cannot compete at present with Europe. But I am sure the time will come when we can. I have unlimited confidence in American brains. Industrial chemical investigation is no less difficult, no less honorable than purely scientific research. If any investigator in pure science doubts this let him try his hand at cracking some technical nut. Let him, for instance, get up a profitable process for making sodium permanganate for our colleague, Mr. Tyrer. \* \* \* What we need now in this country is the establishment of departments of chemical engineering in our larger colleges. \* \* To understand the chemistry of manufacturing is one thing, to be able to handle a chemical reaction mechanically is quite another matter."

Mr. Mond responded for the guests, he said:

"I feel proud that while so many miles from home I am yet no stranger among you. \* \* Professor Austen has remarked that investigation in technical chemistry is quite as difficult as investigation in pure science. There is, however, this great difference that investigation in

pure science bears fruit for centuries to come. Every discovery of new truth is an increase of knowledge and is a benefit to humanity. Technical matters come and go and make room for more perfect methods as time goes on. It is therefore true that a man who devotes himself to pure science deserves the gratitude of future generations as well as his own. We live more for our children and grandchildren than for ourselves, so we cannot do too much in encouraging men who are ready to devote their lives to the betterment of the future. It is extremely natural that in an immense country like this—but it is not right to call it a country or a continent; it is a hemisphere; it is half of this globe—that the few who develop this branch of science shall have little time to think of posterity. In looking at the magnificent institutions that have grown up in this country for the study of science I have very little doubt that the time is not far distant when very many of you will appreciate the importance of pure science more than you have ever done before, and the time will not be far distant when the number will be large enough to meet the wishes of men of science among you."

Mr. W. H. Nichols responded for the Chemical Manufacturers. He said:

"That knowledge is power is true, but how can it be power without the application of it, and how can we have the application without the engineer. \* \* \* There is one other thing in which we can imitate our friends on the other side of the water to advantage, and that is the way in which they come together and compare notes, and receive from one another benefits from the experience each has attained. In this country we have not grown enough to know not to be afraid of each other, and the manufacturing chemist of the United States is hiding his head in the sand like the ostrich \* \* \* In the census of 1890 it was ascertained that there were 1626 manufacturing establishments in the United States. They employed a capital of over one hundred and sixty-eight million dollars, and hired property of the value of twelve million dollars, employing in the aggregate nearly 44,000 persons, and paying a total wage of more than twenty-five million dollars. I desire to call the attention of our guests to one or two facts connected with these employes. Of the total number a little less than 4,000 were females, but only 346 were children. That is one of the best statements I can make to show the condition of the manufacturing industry that it has been necessary to employ only 346 children."

The arrangements for the banquet were in the hands of a committee with J. H. Wainwright as chairman. They were well planned and the occasion was a most enjoyable and profitable one.

E. H.

*Errata.*—Page 759, October Number, in the table headed " $\text{MoO}_3$  in sample 10 Phosphomolybdate" the line Doolittle (Job) 90.47, 93.05, 95.80, should read Doolittle (Job) 89.88, 92.45, 95.18.

---

### A TRIBUTE TO PASTEUR.<sup>1</sup>

A FEW weeks ago, one of the foremost scientists of the present century passed into the great beyond. Louis Pasteur, although a master mind in physics and geology, was preeminently a chemist, therefore it behooves our Society to express its regrets at the great loss sustained not only by France, but which the whole civilized world is obliged to bear. Men like Pasteur, whose life was spent in disseminating broad principles of truth, in alleviating pain, in mitigating epidemic diseases and in exterminating parasites whose activity threatened ruin to the agriculturists, cannot be narrowed down as belonging to one country; but on the contrary are veritable cosmopolites, deservedly honored and venerated by every nation.

It is not my intention to give a sketch of the life of Pasteur, but simply to call your attention, in a brief way, to some of his most important contributions to science and the effects produced. The one, that undoubtedly tended towards moulding his thoughts in the direction to which he devoted his best years was to combat the idea of Heterogenesis and it may truthfully be said that he succeeded in making it untenable by incontestable evidence in support of his theory, that: "The living organized ferments spring only from similar organisms likewise endowed with life; and that the germs of these ferments exist in a state of suspension in the air or on the exterior surface of objects." This not only disproved Fremy's Hemi-organism hypothesis but also Liebig's assertion that "The cause of fermentation is the internal molecular motion, which, in the course of decomposition, is communicated to other matter in which the elements are connected by very feeble affinity." Pasteur, by means of most thorough and extensive research, from 1857-61, simply forced the attention of everybody to the physiological side of the subject, and by absolutely unimpeachable evidence, proved that Schwann's views are correct. Of the investigation, both synthetical and analytical, it is impossible to speak otherwise than in terms of the highest admiration. Even the purely critical portion of Pasteur's work would be enough to immortalize his name. His theory, "That the chemical act of fermentation is

<sup>1</sup> Read before the Cincinnati Section, Oct. 15th.

a correlative phenomenon of a vital act, beginning and ending with it," notwithstanding the thousands of experiments since made by him and other investigators remains unshaken and is to-day the firm basis of all ideas respecting fermentation. Pasteur's researches, by their precision, the care taken to avoid all sources of error, and his rigorous exactness, removed every suspicion of the intervention of germs brought from without or pre-existing in the liquid operated on, a difficulty on which all discussions between heterogenists and panspermists had heretofore turned. By means of the organic corpuscles of dust mixed with amorphous ones, obtained by filtering air through a gun-cotton plug and showing that their absence prevented sterilized fluids from fermenting, but their presence would cause it to set in, Pasteur elevated a hitherto merely observed phenomenon to a scientific basis. His experiments with the forty flasks of must, to show that the ferments which cause the fermentation in the vintage tube, must come from the exterior and not the interior of the fruit, as well as those made to discover quantitatively the germs in the air, are famous.

Pasteur's signal success in counteracting the effects of Pebrine which threatened to destroy the silk industry of France and Italy, not only saved thousands from absolute ruin but taught the people that infectious diseases could be combated by a most novel method. Consequently his efforts toward suppressing the ravages produced by chicken cholera and splenic fever met with less popular prejudice. While experimenting on chicken cholera he produced cultures of varying degrees of virulence by permitting sufficiently long intervals to elapse between the impregnation of one culture with the microbe of the preceding. Furthermore, he proved that each culture of attenuated virulence reproduced the virulence of that which had served as the starting point; concluding from these experiments that the oxygen of the air was the possible cause of the attenuation. When fowls had been rendered sufficiently ill by the attenuated virus which the vital resistance arrested in its development, immunity from the original disease arose. Perhaps one of the most brilliant triumphs achieved by Pasteur consisted in taking advantage of the morphological changes taking place in the Anthracoid

microbe. He prevented it from producing corpuscle germs, kept it while in this condition in contact with oxygen, days, weeks, and months, and thus produced a series of attenuated virulences. With this vaccine he practically exterminated the splenic or carbuncular disease throughout France.

To Pasteur we owe nearly all of our knowledge of the relations between the optical activity and crystalline form in tartaric acid. He showed that enantimorphism depended upon hemihedral forms of the rhombic system. His experiments in this direction led to the discovery of physiological asymmetry and paved the way for the study of elective fermentation. He proved that substances chemically and physically the same save in their opposite rotatory power can serve in one case as nutrients to certain organisms and in the other are worthless as such; and that only certain geometrical forms can serve the requirements of the cells. Thus we see Pasteur as one of the pioneers in the field of stereochemistry.

His successful method of counteracting rabies, his untiring labors in the interest of suffering humanity up to the time of his death forcibly recalls Tyndall's letter, written as far back as 1876. "For the first time in the history of science, we are justified in cherishing confidently the hope that, as far as epidemic diseases are concerned, medicine will soon be delivered from empiricism and placed on a real scientific basis; when that great day shall come, humanity will, in my opinion, recognize the fact that the greater part of its gratitude will be due to you."

Believe me ever faithfully yours,

JOHN TYNDALL.

France can well be proud of such sons as Lavoisier and Pasteur. Generations to come will recognize in their labors the possibility of unveiling, by means of conscientious scientific research, nature's most carefully treasured secrets.

Indeed Longfellow must have had such men in mind when he wrote,

"Lives of great men all remind us  
We can make our lives sublime,  
And, departing leave behind us  
Footprints on the sands of time."

ALFRED SPRINGER.

---



# Index to Vol. XVII, 1895.

<b>A</b> BSORBENT blocks.....	472
Acetanilide, identification of.....	933
Acetic acid and benzene, formation of layers in mixtures of.....	932
Acetic acid in vinegar.....	741, 834
Acetone, improvement in manufacture of.....	187
Air, analysis of Cleveland.....	105
Alkaloids, acedimetric estimation of vegetable.....	822
Allylmalonic, allylacetic and ethylidenepropionic acids, behavior when boiled with caustic soda.....	I
Aluminum and iron, separation of.....	931
Ammonium citrate solution, preparation of.....	47
ANDREWS, LAUNCELOT. On the Analysis of Alloys of Lead, Tin, Antimony and Arsenic.....	869
ANDREWS, W. H. See Campbell, E. D.	
ANDREWS, W. H. A Cheap Form of Self-Regulating Gas Generator.....	304
Anthracene series, experiments in.....	354
Antimonial and arsenical poisoning, a case of.....	667
Antimony, arsenic, tin and lead alloys, analysis of.....	869
Antimony, precipitation from tartar emetic.....	87
Argon, 219, 421; compounds of, 422; use in thermometry.....	477
Arsenical and antimonial poisoning, a case of.....	667
Arsenic, antimony, tin, and lead alloys, analysis of.....	869
Arsenic in glycerol.....	883
Asphalt, analysis of.....	55
ATKINSON, ELIZABETH A., and Edgar F. Smith. The Separation of Iron from Beryllium.....	688
Atomic weights, report of committee on.....	201
AUCHY, GEORGE. The Volumetric Estimation of Manganese.....	943
Austin, Peter T., and W. A. Horton. A Convenient Form of Universal Hand-Clamp.....	611
AUSTIN, PETER T., and W. Homer Broadhurst. Absorbent Blocks.....	472
<b>B</b> ACHMAN, IRVING A. Improved Methods of Water Analysis, 296: Chemical Brick for Glover Towers.....	360
Bacilli, Composition of.....	605
Banquet to Messrs. Mond and Tyrer.....	997
Barium Hydroxide Solution as an absorbent for carbon dioxide.....	247
Barley, Proteids of.....	539
BARTON, G. E. Methods for the Examination of Glycerol for use in the Nitroglycerol Manufacture, 277; Arsenic in glycerol.....	883
BASKERVILLE, CHAS. Reactions between Copper and Concentrated Sulphuric Acid See also Venable, F. P.....	904
BASSETT, LEWIS L., see Fleck, Hermann.	
Beadle, C. See Cross, C. F.	
BEESON, J. L. A Simple and Convenient Apparatus for Estimating the Water-Holding Power of Soils.....	769
Benzene and acetic acid, formation of layers in mixtures of.....	932
Beryllium. See Glucinum.	
BEVAN, E. J. See Cross, C. F.	
BIGELOW, W. D. Coloring Matter in the California Red Wines.....	213

BLAIR, A. A., and J. Edward Whitfield. Ammonium Phosphomolybdate and the Reducing Action of Zinc in the Reductor .....	747
BLASDALE, WALTER C. On the Physical and Chemical Properties of Some California Oils.....	935
BLOMEN, J. E. Some Practical Points in the Manufacture of Nitroglycerol, 263; On the Manufacture of Soluble Nitrocellulose for Nitrogelatin and Plastic Dynamites.....	411
Bone Black. analysis of, 51; decarbonization of.....	503
Books Received.....	-916, 997
BOOK REVIEWS. A Text-Book of Volumetric Analysis (Schimpf) 69; A Text-Book of Inorganic Chemistry (Newth) 71; Die Maschinellen Hilfsmittel der chemischen Technik (Parnicke) 74; The Elementary Nature of Chlorine, Alembic Club Reprint No. 9 (Sir Humphrey Davy) 74; A Treatise on Industrial Photometry, with Special Application to Electric Lighting (Palaz) 151; Descriptive Inorganic General Chemistry (Freer) 152; A Text-Book of Inorganic Chemistry (Bennett) 243; Qualitative Analysis of Inorganic Substances, 245; Proceedings of the 11th Annual Convention of the Association of Official Agricultural Chemists (Wiley), 330; Bibliography of Acetoacetic Ester and its Derivatives (Seymour), 332; Report on the Extent and Character of Food and Drug Adulteration (Wedderburn), 333; Eighth Annual Report of the Dairy and Food Commissioner of Ohio, 333; First Annual Report of the Commissioner of Agriculture of New York (Schraub), 333; A Compilation of the Pharmacy and Drug Laws of the several States and Territories (Wedderburn), 333; Kräfte der chemischen Dynamik (Stettenheimer), 336; Elements of Qualitative and Quantitative Chemical Analysis (Caldwell), 419; Elementary Qualitative Chemical Analysis (Clowes), 419; Handbuch der Stereochemie (Bischoff), 497; A Text-Book of Organic Chemistry (Bernthsen), 500; Manual of Chemistry (Simon), 501; Cod Liver Oil and Chemistry, 584; The Increase in Weight of Tin and Lead on Calcination, 585; A Text-Book of Chemistry Intended for the use of Pharmaceutical and Medical Students (Sadtlir and Trimble), 656; John Dalton and the Rise of Modern Chemistry (Roscoe), 658; An Elementary Course in Experimental and Analytical Chemistry (Long), 744; Elements of Mineralogy, Crystallography and Blowpipe Analysis (Moses and Parsons), 745; Elements of Modern Chemistry (Green and Keller), 832; Justus Von Liebig, His Life and Work (Shenstone), 833; Principles and Practice of Agricultural Analysis, Vol. I (Wiley), 912; A Hand-Book of Industrial Organic Chemistry (Sadtlir), 914; A Manual of Qualitative Chemical Analysis (Harris), 994; Principles and Practice of Agricultural Analysis, vol. II (Wiley), 995; Laboratory Work in Chemistry (Keiser), 996.	
BOWEN, N. C. The Penetration Machine—An Explanation .....	218
BOYER, CHARLES S. Accuracy of the Dyeing Test, 468; Interpretation of some results in the analysis of extracts of fustic .....	518
Butter, examination for foreign fats.....	719
CALCIUM carbide, properties of .....	306
Calcium sulphite, stalactites and stalagmites .....	242
CAMPBELL, E. D., and W. H. Andrews. The Determination of Nickel in Nickel-Steel .....	125
Cane sugar, determination in presence of glucose, 312; action of hydrochloric and acetic acids on.....	320
Carbides of iron with chromium (molybden and tungsten) .....	791
Chromium, determination in chrome ore.....	327
CLARK, EDMUND. Method of Determining Chromium in Chrome Ore.....	327
Clarke, F. W. Report on Atomic Weights Published during 1894 .....	201
CLARKE, THOMAS, see Venable, F. P.	
Coals, determination of heating effects of, .....	843
Condensation of nitric acid .....	576
Conflagrations, methods of extinguishing.....	137, 251, 361
Copper and concentrated sulphuric acid, reactions between .....	904

Copper, the wet assay for.....	346
Cotton, intended for manufacture of gun-cotton, inspection of.....	783
Craver, H. W. See Noyes, W. A.	
Cross, C. F., E. J. Bevan and C. Beadle. The Furfural-yielding Constituents of Plants.....	286
Cushman, Allerton S., and J. Hayes-Campbell. On the Volumetric Determination of Lead .....	901
DeBENNEVILLE, JAMES S. Two Definite Carbides of Iron with Chromium (Molybdenum and Tungsten) .....	791
DeChalmot, G. On Silicides of Iron .....	923
Dennis, L. M. Gerhard Krüss (Obituary Notice).....	423
DeRoode, Rudolf. Some Facts Observed in the Determination of Phosphoric Acid by the Molybdic Acid Process, 43; The Addition of Calcium Chloride to the Solution of a Fertilizer in the Determination of Potash, 46; On the Preparation of Ammonium Citrate Solution, 47; The Determination of Potash in Kainite, 85; The Oxidation of Organic Matter and the Decomposition of Ammonium Salts by Aqua Regia in Lieu of Ignition in the Determination of Potash in Fertilizers ....	86
De Schweinitz, E. A., and Marion Dorsett. The Composition of the Tuberculosis and Glanders Bacilli.....	605
Diastase, chemical nature of .....	587
Doremus, C. A. The Chemical History of a Case of Combined Antimonial and Arsenical Poisoning.....	667
Dorsett, Marion. See DeSchweinitz, E. A.	
Dorrance, John T. See Noyes, Arthur A.	
DuBois, H. W. See Mixer, C. T.	
Dudley, Wm. L. The Relationship of the Heat of Vaporization of Gases to their Density and Also to their Boiling-Point .....	969
Dulin, R. S. The Wet Assay for Copper.....	346
Dunnington, F. P. An Improved Gas Regulator.....	781
Dyeing test, accuracy of .....	468
HRENPFELD, CHARLES HATCH. A Study of the Chemical Behavior of Tungsten and Molybdenum .....	381
Electrolytic analysis: Separations, 612; determination of ruthenium.....	652
Electrolytic reduction of parinitro compounds.....	855
Electrolytic separations .....	612
Elements, early American arrangement of the.....	947
Explosion pipette, modification of Hinman's .....	771
FATTY acids, separation of solid and liquid.....	289, 740
Ferrates, the.....	760
Ferrocyanides. new indicator for, 473; use of organic bases in preparation of.....	927
Fire extinguishers.....	137, 251, 361
Fleck, Hermann, and Lewis L. Bassett. Reduction with Magnesium Amalgam....	789
Food of the future, the synthetic .....	155
Furfural yielding constituents of plants .....	286
Fustic, interpretations of results in analysis of extracts of .....	518
GARRIGUES, W. E. The Determination of Potash in Manures.....	47
Gas analysis, modification of Hinman's explosion pipette, 771; Determination of methane and hydrogen by explosion.....	986
Gas generator, self regulating, 304; new .....	809
Gas regulator, improved.....	781
Gill, Augustus H. A Modification of Hinman's Explosion Pipette.....	771
Gill, Augustus H., and Samuel P. Hunt. The Determination of Methane and Hydrogen by Explosion .....	986
GLADDING, THOMAS S. The Determination of Sulphur in Pyrites.....	397
Glover towers, chemical brick for .....	360

Glucinum salts, purification of .....	604
Glucinum, separation from iron .....	688
Glucose syrup and grape sugar, acidity of, 402; ash in.....	403
Glucose, use of sulphites in manufacture of.....	281
Glycerol, examination of, 277; arsenic in, 883; occurrence of trimethylene glycol in, 890	
Graphite in pig-iron, determination of .....	873
GRIFFITH, A. B. and Charles Platt. On the Composition of Pelagine.....	877
GROSVENOR, WILLIAM M., JR. Some new Solvents for Perchromic Acid.....	41
Group V of periodic system, action of hydrochloric acid gas upon salts of the elements of, 682; action of haloid acid upon.....	735
Gum-cotton, inspection of cotton intended for manufacture of.....	783
<b>H</b> AND-CLAMP, convenient form of .....	611
HANDY, JAMES O. The Superiority of Barium Hydroxide Solution as an Absorbent in Carbon Determinations in Steel.....	247
HARE, C. L. A New Table for the Qualitative Separation of the Metals of the Iron Group .....	537
HARRIS, EDWARD P. A New Generator ....	809
HARRIS, HARRY B. See Smith, Edgar F.	
HART, EDWARD. On Condensation; and Especially on the Condensation of Nitric Acid, 576; Some Points in the Distillation of Nitric Acid, 580; Note on the Purification of Glucinum Salts .....	604
HAYES-CAMPBELL, J. See Cushman Allerton S.	
HEATH, G. L. The Estimation of Sulphur in Refined Copper.....	814
Heat of vaporization of gases, relation to density and boiling-point.....	969
Helium .....	421
HIBBARD, P. L. Quick Estimation of Starch.....	64
HIBBS, JOS. G. See Smith, Edgar F.	
HILLEBRAND, W. F. Warning Against the Use of Fluoriferous Hydrogen Peroxide in Estimating Titanium.....	718
HINDS, J. I. D. A New Hydrogen Sulphide Generator (Note).....	420
HITCHCOCK, FANNY R. M. The Tungstates and Molybdates of the Rare Earths. 483, 520	
HOCHSTETTER, ROBERT W. See Hoffman, Lewis William.	
HOFFMAN, LEWIS WILLIAM, and Robert W. Hochstetter. A New Form of Water-Oven and Still.....	122
HORNE, W. D. The Rapid and Accurate Analysis of Bone-Black, 51; The Decarbonization of Bone Black .....	503
HORTON, H. E. The Use of Sulphurous Acid (HNaSO <sub>3</sub> ) in the Manufacture of Glucose Syrup and Grape Sugar, 281; Alkali and Sulphurous Acid Processes Used in the Manufacture of Starch from Corn, 68; Acidity of Glucose Syrup and Grape Sugar, 402; Ash in Glucose Syrup and Grape Sugar .....	403
HORTON, W. A. See Austin, Peter T.	
Hot air motor.....	494
HYDE, F. S. Scheme for the Identification of Acetanilide, Phenacetine, Quinine Sulphate, etc .....	933
Hydrogen and methane in the atmosphere, 801; determination by explosion.....	986
Hydrogen peroxide sometimes contains fluorine .....	718
Hydrogen sulphide generator, a new .....	420
Illuminating Apparatus .....	496
Indirect analysis of mixtures containing a common constituent.....	466
Iron and aluminum, separation of .....	931
Iron and titanio acid, volumetric determination in ores .....	878
Iron group, qualitative analysis of metals of.....	537
Iron in iron ores, Zimmerman-Reinhardt method for determination of.....	405
Iron, separation from glucinum.....	688
Iron, silicides of.....	923

<b>JEWETT, FRANK F.</b> An Arrangement for Washing Precipitates with Boiling Water.....	517
<b>KEBLER, LYMAN F.</b> Acidimetric Estimation of Vegetable Alkaloids.....	822
<b>KILGORE, B. W.</b> The Determination of Phosphoric Acid by the Molybdate-Magnesia Method and by Volumetric Method, 941; On the Estimation of Phosphoric Acid by Titration of the Ammonium Phosphomolybdate Precipitate with Standard Alkali .....	950
<b>KONINGH, L. DE.</b> Separation of Solid and Liquid Fatty Acids.....	740
<b>KRUG, WILLIAM H.</b> The Determination of Tannin by Metallic Oxides.....	811
<b>KRÜSS, GERHARD.</b> (Obituary Notice).....	423
<b>LANDIS, EDWARD K.</b> The Indirect Analysis of Mixtures Containing a Common Constituent .....	466
Lard analysis, phosphomolybdic acid test applied to .....	33
Lard, examination for impurities.....	723
Lead, tin, arsenic, and antimony alloys, analysis of .....	869
Lead, volumetric determinations of.....	901
<b>LEEDS, ALBERT R.</b> Acetic acid in vinegar.....	741
<b>LENHER, VICTOR.</b> Sulphiodide of Lead.....	511
<b>LINEBARGER, C. E.</b> On Some Experiments in the Anthracene Series, 354; On the Reaction Between Zinc Sulphate and Potassium Hydroxide, 358; On the Vapor Tensions of Mixtures of Volatile Liquids, 615, 690; On the Formation of Layers in Mixtures of Acetic Acid and Benzene.....	932
<b>LONG, J. H.</b> On Certain Phenomena Observed in the Precipitation of Antimony form Solutions of Potassium Antimonyl Tartrate, 87; Obituary Notice of Mark Powers, 586; Obituary Notice of Lothar von Meyer.....	664
<b>LUNGE, G.</b> On the Estimation of Sulphur in Pyrites.....	181
<b>MCCELROY, K. P.</b> Note on the Estimation of Iron and Alumina in Phosphates....	260
<b>McKENNA, C. F.</b> Obituary Notice of Dr. Gideon E. Moore .....	659
<b>MCPHERSON, WILLIAM.</b> See Weber, H. A.	
<b>MCTAGGART, J. R.</b> See Noyes, W. A.	
<b>MABERY, CHARLES F.</b> An Examination of the Atmosphere of a Large Manufacturing City .....	105
Magnesium amalgam, reduction with .....	789
Manganese, determination of, 341; volumetric estimation of .....	943
<b>MASON, W. P.</b> Henry Bradford Nason (Obituary Notice).....	339
<b>MATTHEWS, J. MERRITT.</b> See Smith, Edgar F.	
Methane and hydrogen, determination by explosion.....	986
Methane and hydrogen in the atmosphere .....	801
<b>MEYER, FRED L.</b> See Smith, Edgar F.	
Meyer, Lothar von (Obituary Notice).....	664
<b>MITCHELL, W. L.</b> See Wells, H. L.	
<b>MIXER, C. J., and H. W. DuBois.</b> The Zimmermann-Reinhardt method for the Determination of Iron in Iron Ores .....	405
Molding-sand.....	502
Molybdenum and tungsten, chemical behavior of....	381
Molybdenum carbide .....	421
Molybdates of rare earths.....	483, 520
<b>MUNROE, CHARLES E.</b> Inspection of Cotton for use in the Manufacture of Gun-cotton .....	783
<b>NASON, HENRY BRADFORD.</b> Obituary Notice.....	339
Nickel in nickel steel, determination of.....	125
Nitric acid, condensation of, 576; points in distillation of.....	580
Nitrocellulose, manufacture of soluble .....	411
Nitrogen, determination in fertilizers containing nitrates.....	567
Nitroglycerol, manufacture of.....	263

<b>NORTON, THOMAS H.</b> The Contributions of Chemistry to the Methods of Preventing and Extinguishing Conflagration .....	137, 251, 361
<b>NOTES.</b> Argon: A new constituent of the atmosphere, 219; calcium sulphite, stalactites and stalagmites, 242; an improvement on the Dangles laboratory lamp, 337; spurting in cupellation, 338; a substitute for hydrogen sulphide, 338; a new hydrogen sulphide generator, 420; molybdenum carbide, 421; the gas contained in uraninite, 421; compounds of argon, 422; molding sand, 502; determination of acetic acid in vinegar, 834; the banquet to Messrs Mond and Tyrer, 997.	
<b>Noyes, Arthur A., and John T. Dorrance.</b> The Electrolytic Reduction of Paranitro Compounds in Sulphuric Acid Solution.....	855
<b>NOYES, ARTHUR A., and Willard H. Watkins.</b> The Occurrence of Trimethylene Glycol as a By-Product in the Glycerol Manufacture .....	890
<b>NOYES, W. A., and J. S. Royse.</b> The Volumetric Determination of Phosphorus in Steel and Cast Iron.....	129
<b>NOYES, W. A., J. R. McTaggart and H. W. Craver.</b> The Determination of the Heating Effects of Coals .....	843
<b>OBITUARY NOTICES.</b> Henry Bradford Nason, 339; Gerhard Krüss, 423; Mark Powers, 586; Gideon E. Moore, 659; Lothar Von Meyer, 664; Louis Pasteur.....	1000
Oils, physical and chemical properties of California.....	935
Organic matter in fertilizers, oxidation of by aqua regia.....	86
<b>OSBORNE, THOMAS B.</b> The Proteids of the Rye Kernel, 429; The Proteids of Barley, 539; The Chemical Nature of Diastase .....	587
<b>PASTEUR, Tribute to (obituary notice)</b> .....	1000
<b>PECKHAM, S. F.</b> The Asphalt Question.....	55
Pelagine, composition of.....	877
<b>Pemberton, H., Jr.</b> The Determination of Phosphoric Acid.....	178
Penetration machine, an explanation .....	218
Perchromic acid, new solvents for.....	41
Periodides of pyridine .....	859
Periodic law, modified arrangement of the elements, 75; early American arrangement of the elements.....	947
Periodides, the .....	775
Phenacetine, identification of.....	933
<b>PHILLIPS, FRANCIS C.</b> On the Possibility of the Occurrence of Hydrogen and Methane in the Atmosphere, 801; The Evolution Method for the Determination of Sulphur in White Cast-Iron .....	891
Phosphates, estimation of iron and alumina in.....	260
Phosphoric acid, determination by molybdic acid process, 43; determination of, 178; determination of small quantities by citrate method, 513; reducing action of zinc on ammonium phosphomolybdate, 747; in soils estimation of, 925; determination by molybdate magnesia and volumetric methods, 941; determination by titration of ammonium phosphomolybdate precipitate with alkali.....	950
Phosphorus in steel and cast-iron, volumetric determination of .....	129
<b>PLATT, CHARLES.</b> See Griffith, A. B.	
Potash, determination of kainite, 85; oxidation of organic matter in fertilizers in determination of, 86; determination as platinichloride.....	453
Potash in fertilizers, addition of calcium chloride in determination of.....	46
Potash in manures, determination of .....	47
<b>POWERS, MARK.</b> (Obituary Notice) .....	586
<b>PRESCOTT, A. B., and P. F. Trowbridge.</b> Periodides of Pyridine .....	859
<b>PRESCOTT, A. B.</b> The Periodides .....	775
Proteids of the rye kernel.....	429
Pyridine, periodides of.....	859
Pyrites, estimation of sulphur in.....	772

<b>QUALITATIVE analysis of metals of iron group.....</b>	<b>537</b>
QUINAN, W. R. Some Physical Aspects of the New Gas Argon, the Ideal Thermometrical Substance .....	477
Quinine sulphate, identification of.....	933
<b>RAWLING, CHARLES Q. Note on a Molding Sand.....</b>	<b>502</b>
ROSELL, CLAUDE A. O. The Ferrates.....	760
ROYSE, J. S. See Noyes, W. A.	
RUNYAN, E. G., and H. W. Wiley. On the Determination of Small Quantities of Phosphoric Acid by the Citrate Method .....	513
Ruthenium, electrolytic determination of.....	652
Rye kernel, proteids of .....	429
<b>SAUER, EWALD. Some New Laboratory Apparatus.....</b>	<b>494</b>
SHERMAN, H. C. The Determination of Nitrogen in Fertilizers Containing Nitrates, 567	567
SHIMER, P. W. Note on the Determination of Zinc, 310; the Determination of Graphite in Pig-Iron .....	873
SHIVER, F. S. On the Standardization of Sulphuric Acid.....	351
SMITH, EDGAR F. and Daniel L. Wallace. Electrolytic Separations .....	612
SMITH, EDGAR F. and Fred L. Meyer. The Action of Haloid Acids in Gas Form upon the Salts of Elements of Group V of the Periodic System.....	735
SMITH, EDGAR F. and Harry B. Harris. The Electrolytic Determination of Ruthenium, 652; the Action of Phosphorus Pentachloride upon the Dioxides of Zirconium and Thorium.....	654
SMITH, EDGAR F. and Joseph G. Hibbs. Action of Hydrochloric Acid Gas upon Salts of the Elements of Group V of the Periodic System .....	682
SMITH, EDGAR F. and J. Merritt Matthews. Uranium Oxynitride and Uranium Dioxide .....	686
SMITH, EDGAR F. See Atkinson, Elizabeth A.	
SNYDER, HARRY. The Action of Mineral Acids upon Soils.....	148
Soils, action of mineral acids upon, 148; apparatus for estimating the water holding power of.....	769
SPENZER, JOHN G. On the Behavior of Allylmalonic, Allylacetic and Ethylidenepropionic Acids when Boiled with Caustic Soda Solutions .....	1
SPRINGER, ALFRED. A Tribute to Pasteur .....	1000
SQUIBB, E. R. Improvement in the Manufacture of Acetone .....	187
Starch, quick estimation of, 64; processes used in manufacture from corn.....	68
Still for the laboratory, convenient .....	917
STONE, GEO. C. The Volumetric Determination of Zinc and a New Indicator for Ferricyanide.....	473
Sugar houses, estimation of extraction in.....	920
Sulphiodide of lead .....	511
Sulphur, estimation in pyrites.....	181, 397
Sulphur, estimation in refined copper.....	814
Sulphur in white cast-iron, determination of.....	891
Sulphuric acid and copper, reactions between concentrated.....	904
Sulphuric acid, standardization of .....	351
<b>TANNIN, determination by metallic oxides .....</b>	<b>811</b>
Tellurium, estimation in copper bullion, 280; separation from copper residues, etc. 849	849
TENNILLE, GEORGE T. The Phosphomolybdic Acid Test as Applied to Lard Analysis .....	33
THOMAS, W. S. Methods for the Determination of Manganese.....	341
Thermometry, Use of Argon in.....	477
Tin, lead, arsenic, and antimonious alloys, analysis of.....	869
Titanic acid and iron, volumetric determination in ores .....	878
Titanium, warning against use of fluoriferous hydrogen peroxide in estimating.....	718
Trimethylene glycol, occurrence in glycerol .....	890
TROWBRIDGE, P. F. See Prescott, A. B.	

TRUBEK, M. On the Estimation of the Extraction in Sugar Houses.....	920
Tungsten and molybdenum, study of chemical behavior of.....	381
Tungstates of rare earths .....	483, 520
TWITCHELL, E. The Separation of Solid and Liquid Fatty Acids.....	289
URANIUM oxynitride and dioxide.....	686
VAPOR tensions of volatile liquids.....	615, 690
VENABLE, F. P. A Modified Arrangement of the Elements Under the Natural Law 75; the Chlorides of Zirconium, 842; An Early American Arrangement of the Elements .....	947
VENABLE, F. P., and Charles Baskerville. Zirconium Sulphite.....	448
VENABLE, F. P., and Thomas Clark. Some of the Properties of Calcium Carbide....	306
Vinegar, acetic acid in.....	741, 834
Volatile liquids, vapor tensions of mixtures of.....	615, 690
Volumetric analysis. Determination of phosphorus in steel and cast-iron. 129; deter- mination of phosphoric acid. 178; the wet assay for copper, 346; standization of sulphuric acid, 351; determination of iron in iron-ores. 405; determination of zinc, 473; impurity in hydrogen peroxide, 718; determination of acetic acid, 741, 834; estimation of vegetable alkaloids, 822; determination of titanio acid and iron in ores, 878; determination of lead, 901; estimation of phosphoric acid in soils, 925; determination of phosphoric acid, 941; estimation of manganese, 943; deter- mination of phosphoric acid.....	950
WALKER, PERCY H. On the Use of Organic Bases in the preparation of Barium and Calcium Ferrocyanides .....	927
WALLACE, DANIEL L. See Smith, Edgar F.	
WAIT, CHARLES E. A Convenient Still for the Laboratory .....	917
Washing precipitates with boiling water, arrangements for.....	517
Water Analysis, improved method of.....	296
Water-oven and still, new form of.....	122
WEBER, H. A. and William McPherson. On the Determination of Cane Sugar in the Presence of Commercial Glucose, 312; On the action of Acetic and Hydrochloric Acids on Sucrose.....	320
WELLS, H. L. and W. L. Mitchell. On the Volumetric Determination of Titanio Acid and Iron in Ores.....	878
WENDER, DR. NEWMAN. The Viscosimetric Examination of Butter for Foreign Fats	719
WESSON, DAVID. The Examination of Lard for Impurities.....	723
WHITEHEAD, CABELL. Estimation of Tellurium in Copper Bullion, 280; Tellurium : Its Separation from Copper Residues with Notes on Some New Reactions.....	849
Paranitro compounds, electrolytic reduction of .....	855
White lead, electrolytic process for manufacture of.....	835
WHITEFIELD, J. EDWARD. See Blair, A. A.	
WILEY, HARVEY W. The Synthetic Food of the Future ... ..	155
See also Runyan, E. G.	
WILLIAMS, C. B. Estimation of Phosphoric Acid in Soils by Double Precipitation with Molybdate Solution and Titration of the Ammonium Phosphomolybdate with Standard Alkali .....	925
WILLIAMS, R. P. An Electrolytic Process for the Manufacture of White Lead .....	835
Wines, coloring matter in California red.....	213
WINTON, A. L. On Some Conditions Affecting the Accuracy of the Determination of Potash as Potassium Platinichloride.....	453
ZINC, determination of, 310; volumetric determination of.....	473
Zinc sulphate and potassium hydroxide, reaction between.....	358
Zirconium and thorium dioxides, action of phosphorus pentachloride upon.....	654
Zirconium, chlorides of.....	842
Zirconium sulphite .....	448







